CCG.

COAL CHARACTERIZATION GROUP.

DEPARTMENT OF CHEMISTRY. St Francis Xavier University.

STUDY ON CHEMICAL DERIVATIZATION AND FTIR SPECTRA OF WESTERN CANADIAN COAL

FINAL REPORT

By

Brian M. Lynch and Lai-Im Lancaster

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Antigonish, Nova Scotia. B2G-1C0.

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ABSTRACT

PhotoAcoustic Infrared Fourier Transform (P A I F T) Spectroscopy has been employed to delineate and compare the stages of artificial and natural oxidation processes for eleven Western Canadian bituminous and sub-bituminous coals using different temperature conditions and modes of oxidation treatment.
Several hundred spectra are in permanently stored files available for manipulative processing.

Various pre- and post-oxidation chemical derivatization treatments and procedures for demineralization of the coal samples were employed to enhance the sensitivity of the detection and assessment of oxidation, and to establish the effects of chemical derivatization on the rates and pathways of oxidation.
Three standardized techniques have been developed to indicate the extent of oxidation in the coals: (i) evaluation of the high-frequency asymmetry of the 1600 cm.-1 band by peak half-width or by (ii) half-peak integrated intensity, or (iii) chemical derivatization by methylation, providing "chemical deconvolution" of the various carbonyl-type functionalities.

A detailed set of pathways for the oxidation processes has been developed which is applicable to oxidations up to 300 degrees Celsius. We have also obtained evidence proving that recent suggestions by Liotta and his co-workers, implying that ether groups are formed at the early stages of oxidation, result from inconsistencies in spectral subtraction procedures.

Computer-controlled subtraction may be used to simulate the spectra of demineralized coals by removal of the mineral-matter spectrum from that of as-received coal. The subtraction process may also be used to enhance the sensitivity of detection and ease of characterization of introduced oxygen functions.

Tests have established the feasibility of compositional analysis of coal blends using P A I F T techniques.

Brief comparisons of the P A I F T spectra and D R I F T (Diffuse Reflectance

Infrared Fourier Transform) spectra of parallel samples lead us to the preliminary conclusion that P A I F T procedures are to be preferred for observations at normal laboratory temperatures. The common impression that P A I F T has poor signal/noise characteristics relative to D R I F T confuses signal level with signal quality. Resolvability with P A I F T, particularly in the carbonyl region, of key significance for assessment of oxidation, is better than with D R I F T.

EXPERIMENTAL SECTION

PROTOCOLS FOR SAMPLE PREPARATION

Received coal samples were ground using a Brinkmann pulverizer system and the -200 mesh fractions were used for further chemical treatment and for spectroscopic examination. Samples were stored in sealed containers at approximately 20 degrees C. All samples for PAIFT measurements were dried at 100 degrees Celsius in a Fisher Vacuum Oven for at least 3 h before examination. Dried samples were stored in sealed vials in desiccators. Samples were packed to constant pressure using a packing device based upon a screw micrometer.

PAIFT SPECTRA

The spectra were acquired using a Bruker IFS110 purge Spectrometer interfaced with a Princeton Applied Research Model 6003/6005 Photoacoustic Spectrometer.

Interferograms were obtained over a spectral range from 4,000 to 400 cm-1 using 128 scans at a nominal resolution of 8 cm-1 with a zero-filling factor of 2, Fourier-transformed and ratioed against the photoacoustic response of a vacuum-dried sample of Fisher C-198 Lampblack Carbon, to provide photoacoustic infrared spectra with encoding at intervals of 4 cm-1.

The interferometer mirror velocity setting was 2, corresponding to a mirror velocity of 0.08333 cm sec-1, and an optical velocity of 0.33333 cm sec-1.

For plotting, the ratioed spectra were smoothed using the computer's smoothing function setting of 4, which uses an eleven-point moving average to weight individual data points.

The spectral files are stored permanently on Memorex hard disks in the unsmoothed mode.

CHEMICAL TREATMENTS

(1) Demineralization

This procedure is based upon that used by the CSIRO (Australia) for Australian coals (see H. R. Brown, R. A. Durie, and H. N. S. Schafer, Fuel, Vol. 38, pp. 295-308 (1959)).

Two grams of the powdered coal (-200 mesh) are heated in refluxing 5M aqueous hydrochloric acid (100 mL) for 1 hour. After cooling, the coal sample is recovered by suction filtration and immersed in 25 % aqueous hydrofluoric acid (100 mL) at 50-55 degrees C for one hour. The coal sample is suction-filtered, washed with water (1 litre) and heated under reflux for a further hour with 5M aqueous hydrochloric acid. the demineralized product is treated by Soxhlet extraction with water until the extract is free of chloride ion. The solid residue is dried under vacuum at 100-105 degrees Celsius.

(2) Methylation

(a modification of the procedure suggested by R. L. Liotta, Fuel, 58, 724 (1979)).

One gram of the powdered coal (-200 mesh) is stirred under nitrogen for 2 hours in 40 % aqueous tetrabutylammonium hydroxide (Aldrich Chemical Company Catalog # 17,878-0)(10 mL) and tetrahydrofuran (Aldrich Chemical Company Gold Label, Catalog # 14,722-2) (10 mL). Iodomethane (2.0 mL) is added and the mixture is stirred for 6 hours in a stoppered, sealed, flask under a nitrogen atmosphere.

The methylation sequence is repeated by addition of identical amounts of the above reagents.

The reaction mixture containing the methylated coal is diluted with methanol (100 mL) and the product is collected by suction filtration, and exhaustively extracted in a Soxhlet apparatus with methanol (300 mL) until the extract is free of iodide ion (approximately 12 hours extraction). The solid residue (methylated coal) is washed thoroughly by suction on a sintered-glass funnel using methanol as wash liquid, air-dried at room temperature, then vacuum dried at 100 degrees Celsius.

The dried product is stored in a screw-top vial in a vacuum desiccator.

TABLE 1

LISTING OF COAL SAMPLES SUPPLIED BY COAL RESEARCH LABORATORY

#	C R L #	Sample description
1.	82-1	Harmer Seam (B.C.) bituminous coal; pit 29 South, raw, uncrushed, unoxidized
2.	82-2	Judy Creek sub-bituminous coal; raw, less than 1/8 inch, stored since 1980
3.	82-3	McIntyre Mines Limited bituminous coal; raw, crushed to 3/8 inch
4.	82-4	Ewin Pass bituminous coal; adit 2, seam 4, naturally oxidized, 20 m. depth
5.	82-5	same as 82-4, 22 m. depth
6.	82-6	Sample 82-1 artificially oxidized for 7 days
7.	82-7	British Petroleum bituminous coal; adit sample, raw, 3/8 inch (900 g)
8.	82-8	Coleman Collieries bituminous coal; raw run-of-mine, crushed (400 g)
9.	82-9	Judy Creek sub-bituminous coal; cleaned, 1/8 inch (500 g)
10.	82-10	Cardinal River bituminous coal; raw coal, lumps to 6 inches, in storage since 1978 (2 kg)
11.	82-11	Harmer seam (B.C.) bituminous coal; raw lumps to 6 inches, in storage since 11/1980 (2 kg)

TABLE 2

ULTIMATE ANALYTICAL DATA ON C R L SAMPLES*

CRL #	Analyses, as received, %				Converted to D M M F Basis, %			L T A, %
	C	H	O	Ash	C	H	O	
1	77.60	3.73	4.67	3.10	80.08	3.85	4.82	11.0
2	38.65	3.17	16.35	38.65	63.53	5.18	26.74	40.0
3	81.65	3.26	3.68	7.60	88.37	3.53	3.98	
4	68.94	3.90	12.31	8.70	75.51	4.27	14.04	12.0
5	70.85	4.31	10.35	10.01	78.73	4.79	11.50	14.0
7	69.72	3.64	4.34	19.40	86.50	4.51	5.38	19.0
8	56.30	3.01	7.22	31.0	82.36	4.36	10.46	35.0
9	55.75	3.80	20.24	14.2	64.98	4.43	25.38	16.0
10	81.29	4.62	5.83	6.20	86.66	4.93	6.22	

*Microanalyses by Schwarzkopf Microanalytical Laboratories, Woodside, New York; low-temperature ash (LTA) determined in-house.

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3	" " " , demineralized, then methylated
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5	" " " , as received & methylated
6	" " " , demineralized, then methylated
7	CRL 82-3 McIntyre Mines Coal, as received & demineralized
8	" " , as received & methylated
9	" " , demineralized, then methylated
10	CRL 82-4 Ewin Pass (20 m) Coal, as received & demineralized
11	" " , as received & methylated
12	" " , demineralized then methylated
13	CRL 82-5 Ewin Pass (22 m) Coal, as received & demineralized
14	" " , as received & methylated
15	" " , demineralized then methylated
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20	" " , as received & methylated
21	" " , demineralized then methylated
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23	" " , as received & methylated
24	" " , demineralized then methylated
25	CRL 82-9 Judy Creek Coal, cleaned, as received & demineralized
26	" " " , as received & methylated
27	" " " , demineralized then methylated
28	CRL 82-10 Cardinal River Coal, as received & demineralized
29	" " , as received & methylated
30	" " , demineralized then methylated
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32	" " , as received & methylated
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REVIEWS, RESULTS, AND DISCUSSION

REMOVAL OF THE INORGANIC CONTRIBUTIONS TO THE INFRARED SPECTRA OF COALS BY CHEMICAL DEMINERALIZATION OR BY SIMULATED DEMINERALIZATION

Western Canadian coals typically contain significant amounts of mineral matter (see the analytical data Table for the current set of samples), and interference of the mineral-matter absorption with the infrared spectral features intrinsic to the coal makes it difficult to establish with confidence such significant points as the content of ether groups in a coal or the substitution pattern of aromatic hydrogen atoms. Removal of the interfering features may be attained by the processes of chemical demineralization of the coal by successive HCl-HF-HCl-H2O treatments, but the very severity of such procedures casts doubt on conclusions about structural features in the original coal matrix.

Bearing this reservation in mind, we have carried out standard chemical demineralization treatments (described on pp.3-4) on the samples of as-received coals, and the PAIFT spectra of the as-received and demineralized coals are compared in Figures 1,4,7,10,13,16,19,22,25,28, and 31.

It is evident from the compared spectra that the features characteristic of kaolinite at approximately 3650, 1100-1000, and 800 cm.-1 are eliminated from the chemically demineralized coals. In addition, for the CRL 82-2 and 82-9 samples (Judy Creek sub-bituminous coals), there are substantial differences in the 1800-1600 cm.-1 absorptions as a result of the liberation of carboxylic acid groups from the basic mineral matter which formed carboxylate salts in the original coals.

The detailed results confirm that comparisons of as-received and chemically demineralized coals render unreliable many assessments of distribution of particular structural features (including such points as the extent of oxidation, the distribution of aromatic hydrogen), and that some normalization or standardization procedure should be undertaken before attempted evaluation of transformations of the coal (for example, oxidations or derivatization by methylation).

As specific illustrations of the difficulties in quantitation arising from mineral-matter interference, and of potential changes in mineral matter composition accompanying a derivatization procedure on the organic component of the coal matrix, comparisons of the spectra of the as-received and chemically

demineralized coal CRL 82-1 in Figure 1 show significant differences in the intensity ratios of the aliphatic C-H stretch and aromatic out-of-plane deformation absorptions for the two samples, casting doubt on any assessments of the fraction of aromatic character of the as-received coal.

Also, although it has been claimed by Liotta and his colleagues that the phase-transfer methylation process as developed by them effects quantitative conversion of all acidic hydroxyl groups, examination of the spectra of the methylated CRL 82-1 samples derived from the as-received coal and the demineralized material (Figures 2 and 3) show that there are residual hydroxyl absorptions, and also that the extent of methylation (as judged from the intensities of aliphatic C-H stretch features relative to the remaining peaks in the spectrum) is greater for the demineralized coal. This probably results from greater accessibility of the demineralized coal to the methylating agent.

Further evidence indicating that the extent of methylation is greater for treatment of the demineralized coal is that the intensity of the resolved carbonyl feature around 1700 cm.-1 is greater in the upper spectrum of Figure 3 than in Figure 2, although this difference could arise from sample variability.

To summarize the data base appearing in Figures 1-33, the chemical demineralization treatment appears necessary for any meaningful comparisons of spectral absorption features characteristic of the organic matrix of the coal. The efficiency of methylation procedures is enhanced by preliminary demineralization.

The availability of digitized spectral files of both as-received and demineralized coals provides the possibility of an artificial generation of the mineral-matter spectrum by appropriate subtraction (see, for example, P. C. Painter and co-workers, Applied Spectroscopy, 35, 102-106 (1981); Fuel, 57, 337-344 (1978); American Laboratory, 12, 19-29 (1980)), and this could be effected with the present data base.

However, if the mineral-matter is dominated by clay minerals, as is the case for the present suite of coal samples, it should be practicable to use the automatic subtraction software of the Bruker ATS program to make proportionate subtractions of a "standard" mineral-matter spectrum from the as-received coals. We have attempted this using a standard kaolinite spectrum, which is a reasonable representation of the mineral matter accompanying these coals

(comparisons of the spectra of the kaolinite standard and of the low-temperature ash materials are presented in Figure 34).

The spectra in the 2000-600 cm.-1 region of the as-received samples and the simulated demineralized coal spectra from the indicated proportionate subtraction of the kaolinite are presented in Figures 35 through 43. There is a good correspondence between the general features of the chemically demineralized and "computer-simulated" demineralized spectra, although there is usually an element of under-subtraction (some residual indications remain from the strong Si-O peaks at 1120 and 1050 cm.-1). However, the significant point about the subtraction procedures is that the proportionality constants in the subtractions are linearly related to the actual (experimental) percentages of ash in the coal samples.

This is shown in the accompanying Table, and in Figure 44.

ASH CONTENT OF CRL SAMPLES CORRELATED WITH KAOLINITE SUBTRACTION

CRL Sample #	Ash (%)	Proportionality constant	
		from simulation	calculated from linear equation
10	6.2	7.0	8.5
3	7.6	10.5	9.7
6	9.8	11.0	11.5
7	19.4	18.0	19.6
8	31.0	29.0	29.3
2	38.9	36.0	35.8

Proportionality constant = 3.34 + 0.837(ash fraction)

Correlation coefficient r = 0.988

Thus, immediate indications of the proportion of mineral matter in the series of supplied samples are provided from direct output of the computer-optimized subtraction procedure.

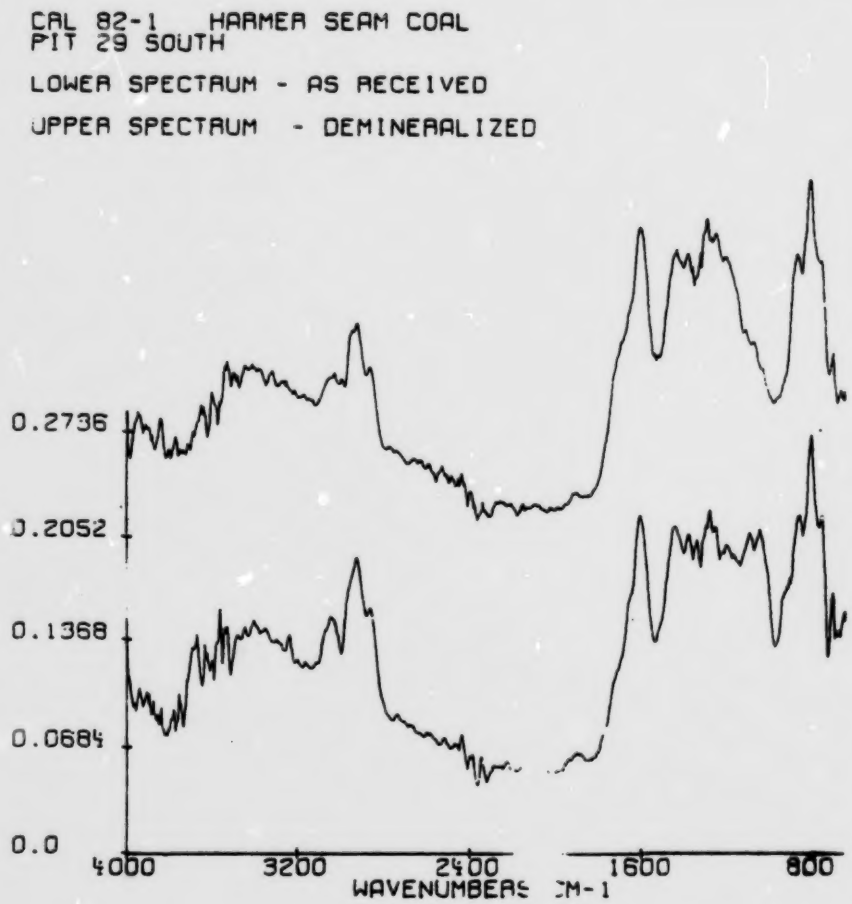

CAL 82-1 HARMER SEAM COAL
PIT 29 SOUTH
LOWER SPECTRUM - AS RECEIVED
UPPER SPECTRUM - DEMINERALIZED
0.2736
0.2052
0.1368
0.0684
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 1

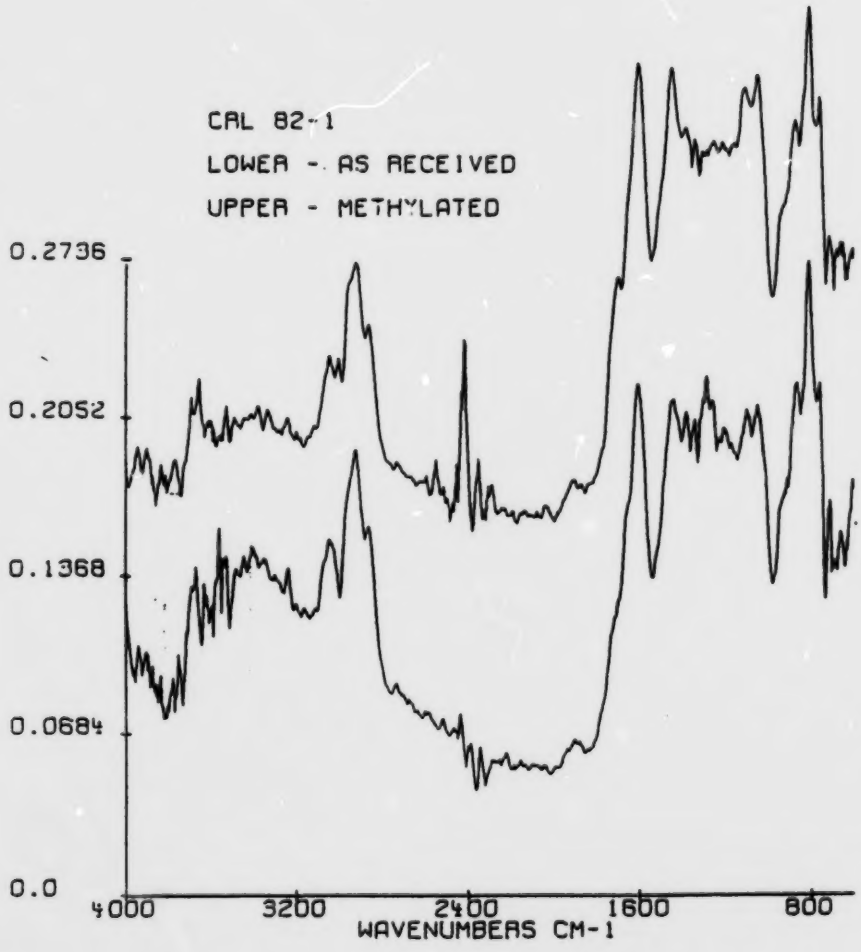

CAL 82-1
LOWER - AS RECEIVED
UPPER - METHYLATED
0.2736
0.2052
0.1368
0.0684
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 2

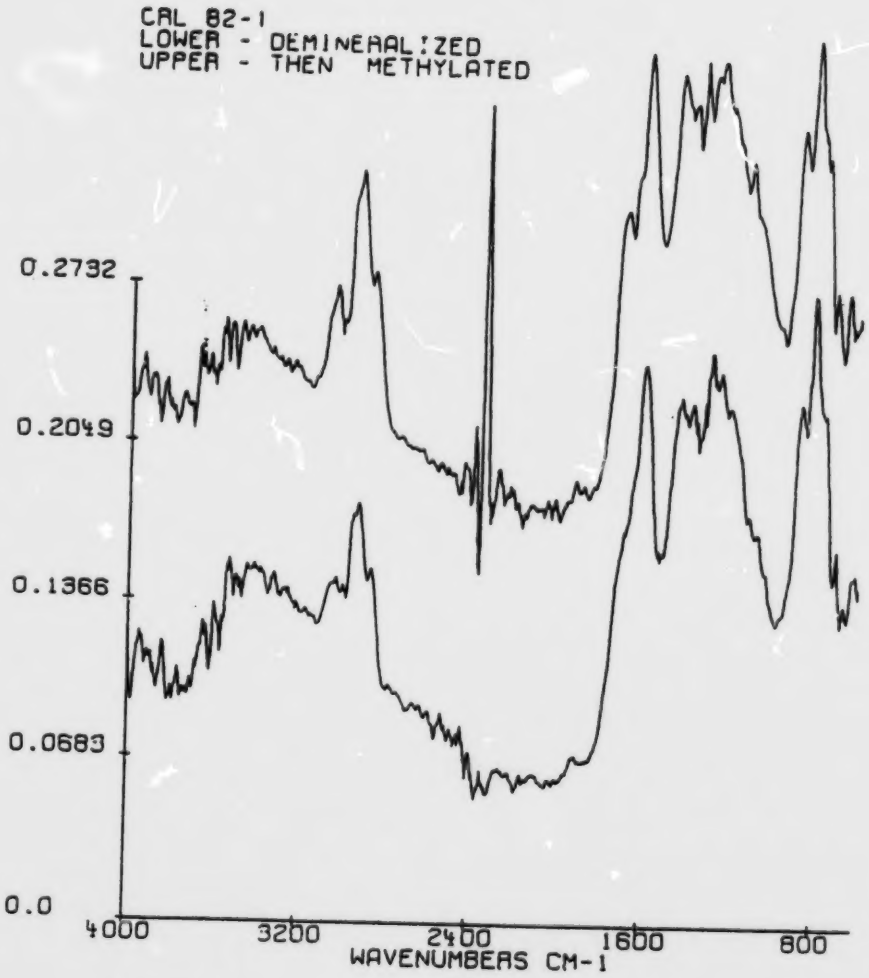

CAL 82-1
LOWER - DEMINERALIZED
UPPER - THEN METHYLATED
0.2732
0.2049
0.1366
0.0683
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 3

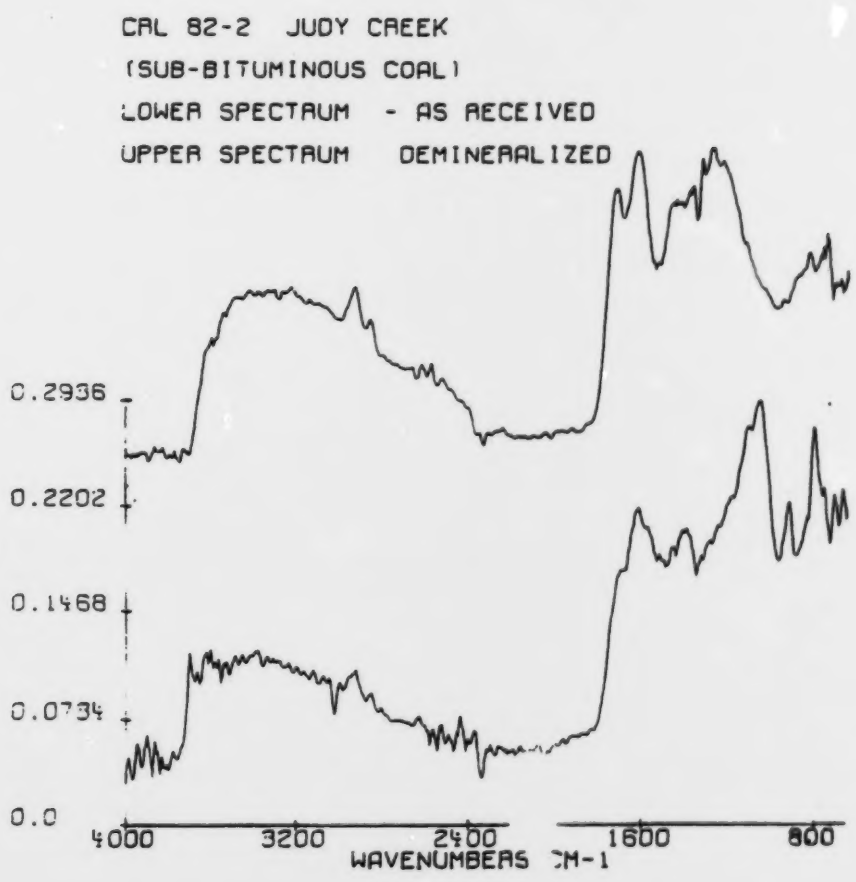

CAL 82-2 JUDY CREEK
(SUB-BITUMINOUS COAL)
LOWER SPECTRUM - AS RECEIVED
UPPER SPECTRUM DEMINERALIZED
0.2936
0.2202
0.1468
0.0734
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 4

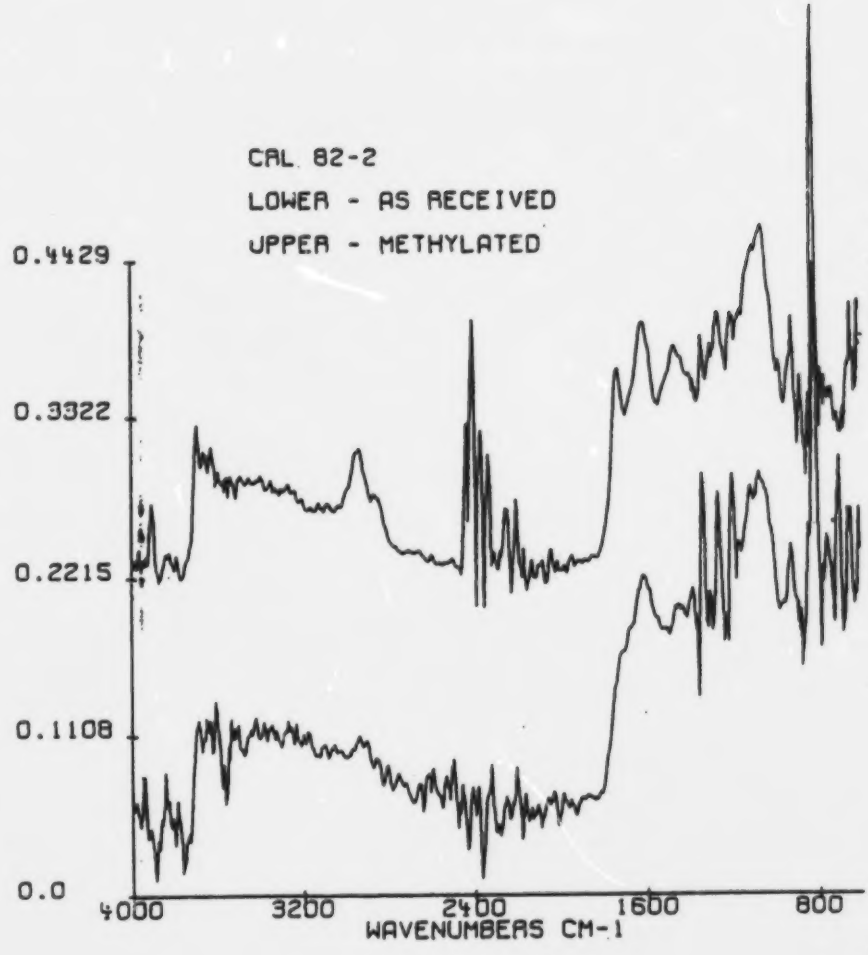

CAL 82-2
LOWER - AS RECEIVED
UPPER - METHYLATED
0.4429
0.3322
0.2215
0.1108
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 5

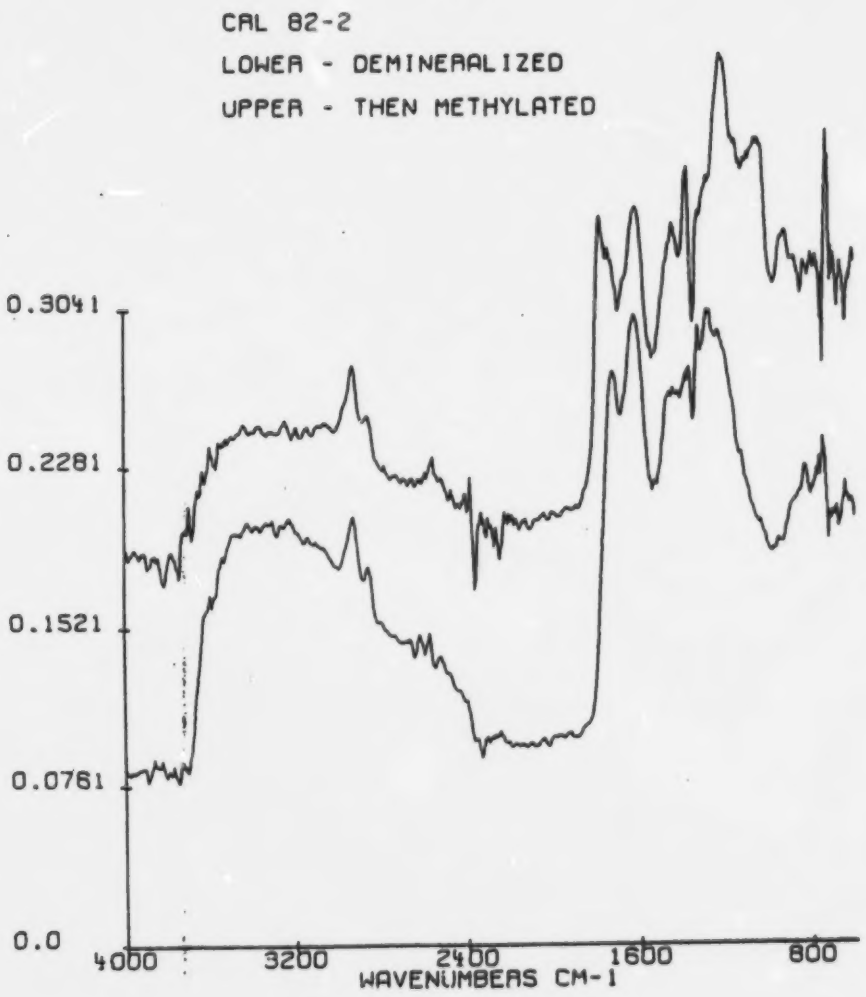

CAL 82-2
LOWER - DEMINERALIZED
UPPER - THEN METHYLATED
0.3041
0.2281
0.1521
0.0761
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 6

CAL 82-3
MCINTYRE MINES
RAW, BITUMINOUS
LOWER SPECTRUM - AS RECEIVED
UPPER SPECTRUM - DEMINERALIZED

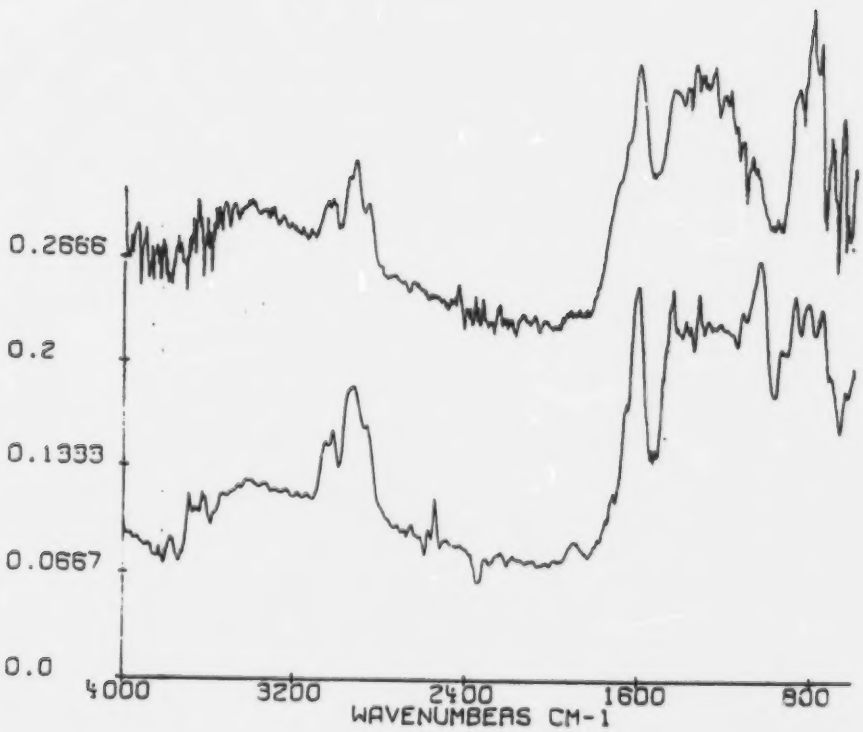


FIGURE 7

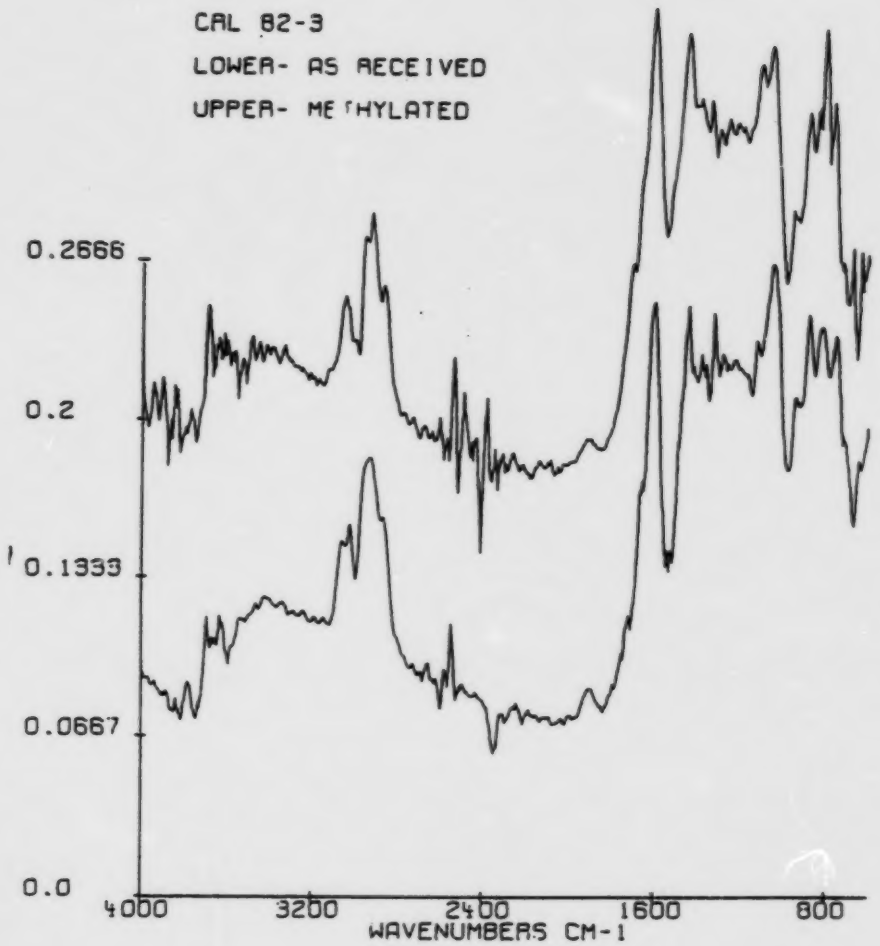

CAL 82-3
LOWER- AS RECEIVED
UPPER- METHYLATED
0.2666
0.2
0.1333
0.0667
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 8

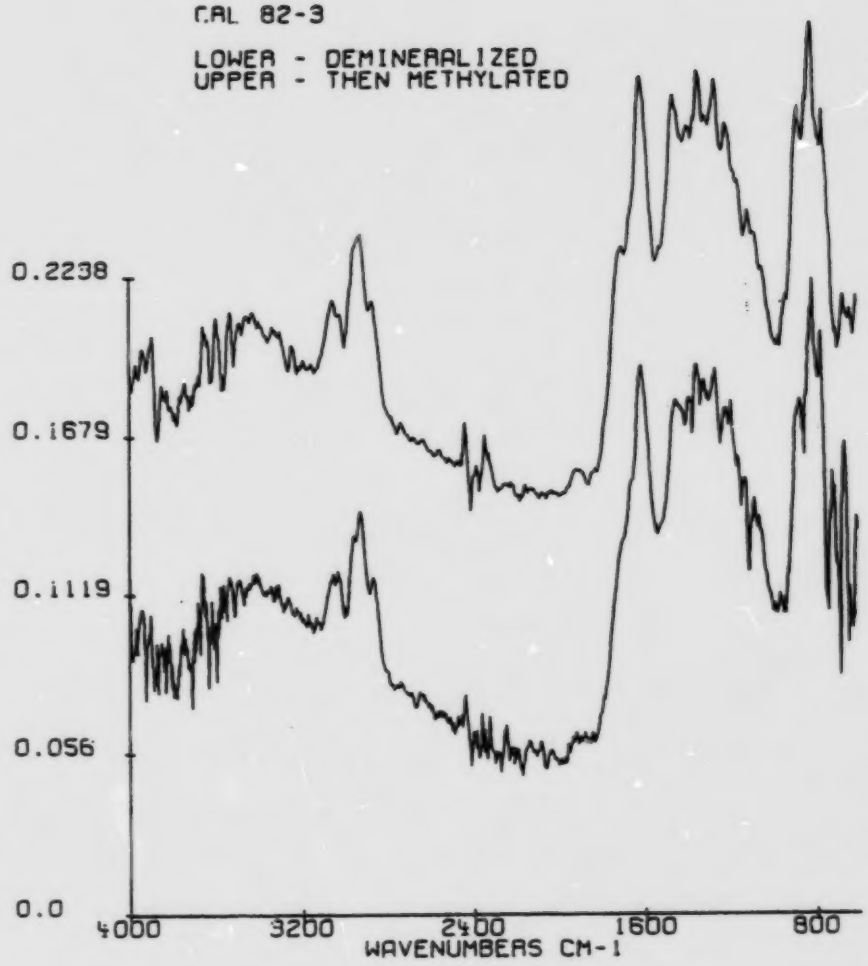

CAL 82-3
LOWER - DEMINERALIZED
UPPER - THEN METHYLATED
0.2238
0.1679
0.1119
0.056
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 9

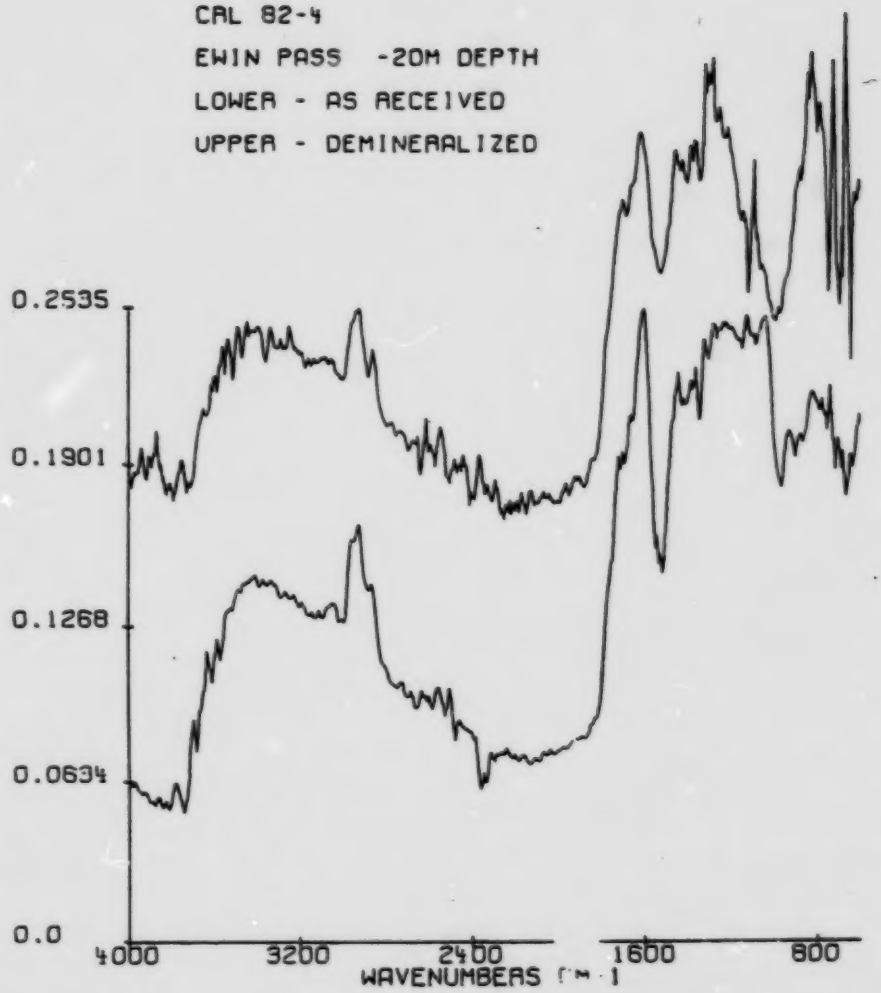

CAL 82-4
EWIN PASS -20M DEPTH
LOWER - AS RECEIVED
UPPER - DEMINERALIZED
0.2535
0.1901
0.1268
0.0634
0.0
4000
3200
2400
1600
800
WAVENUMBERS (cm-1)

FIGURE 10

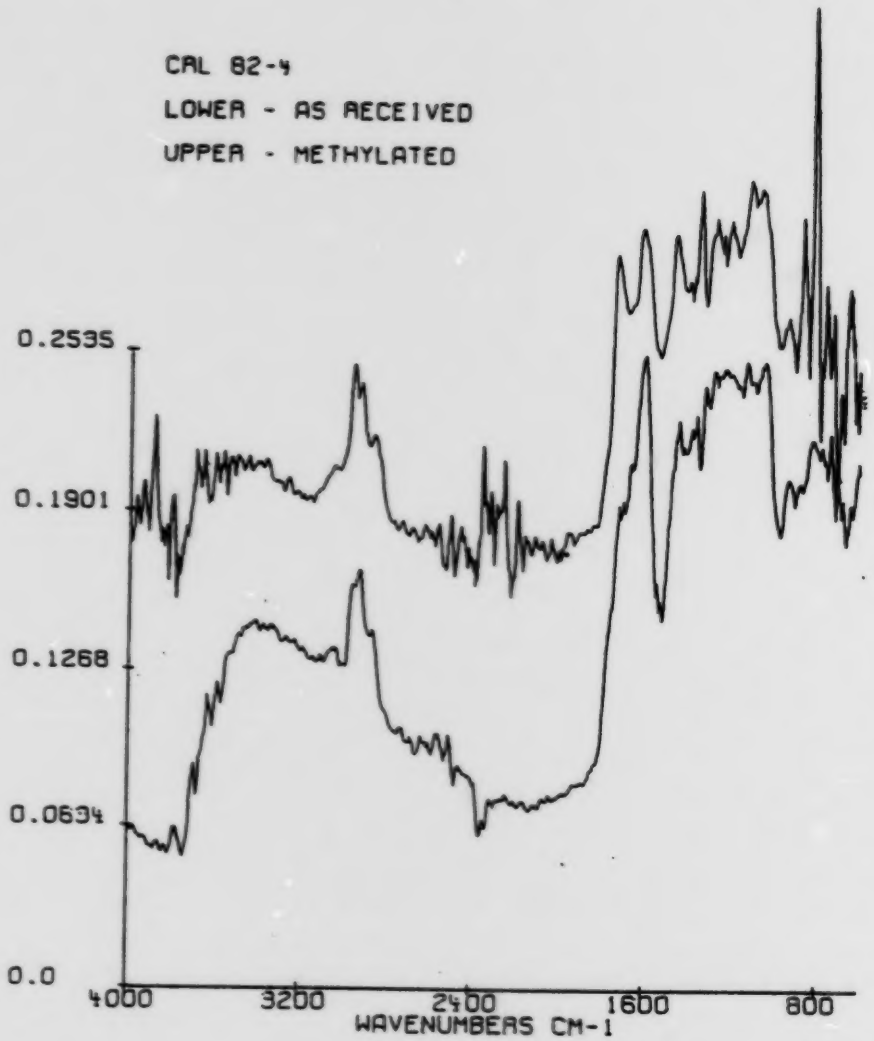

CAL 82-4
LOWER - AS RECEIVED
UPPER - METHYLATED
0.2535
0.1901
0.1268
0.0634
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 11

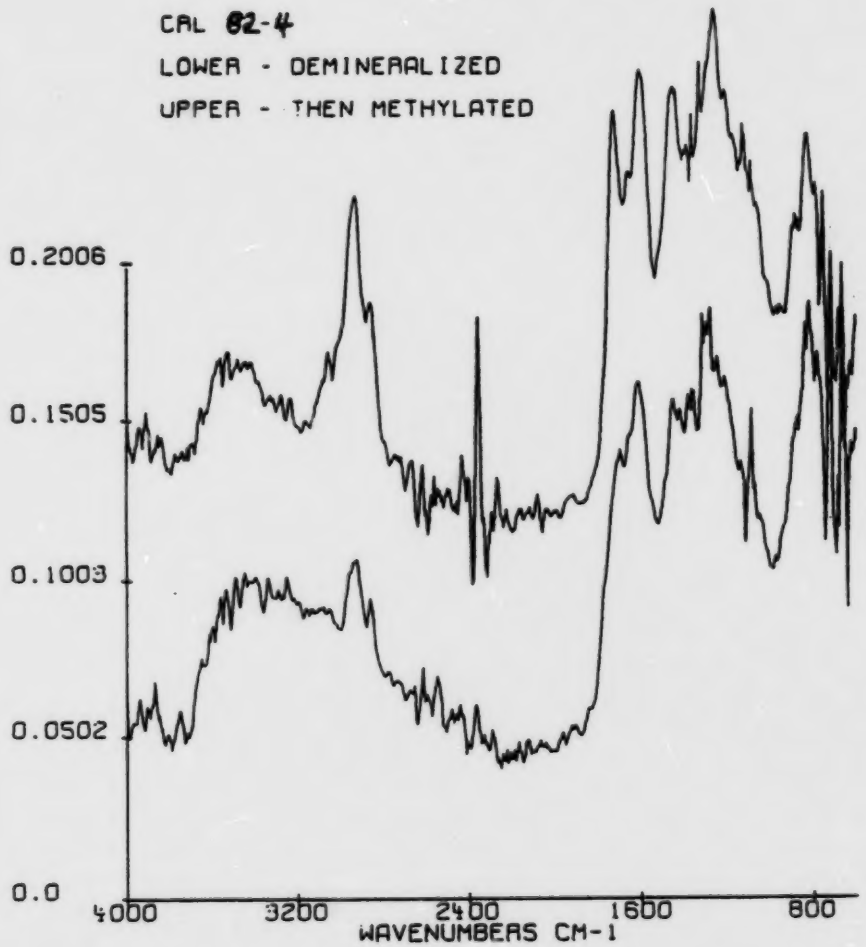

CAL 82-4
LOWER - DEMINERALIZED
UPPER - THEN METHYLATED
0.2006
0.1505
0.1003
0.0502
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 12

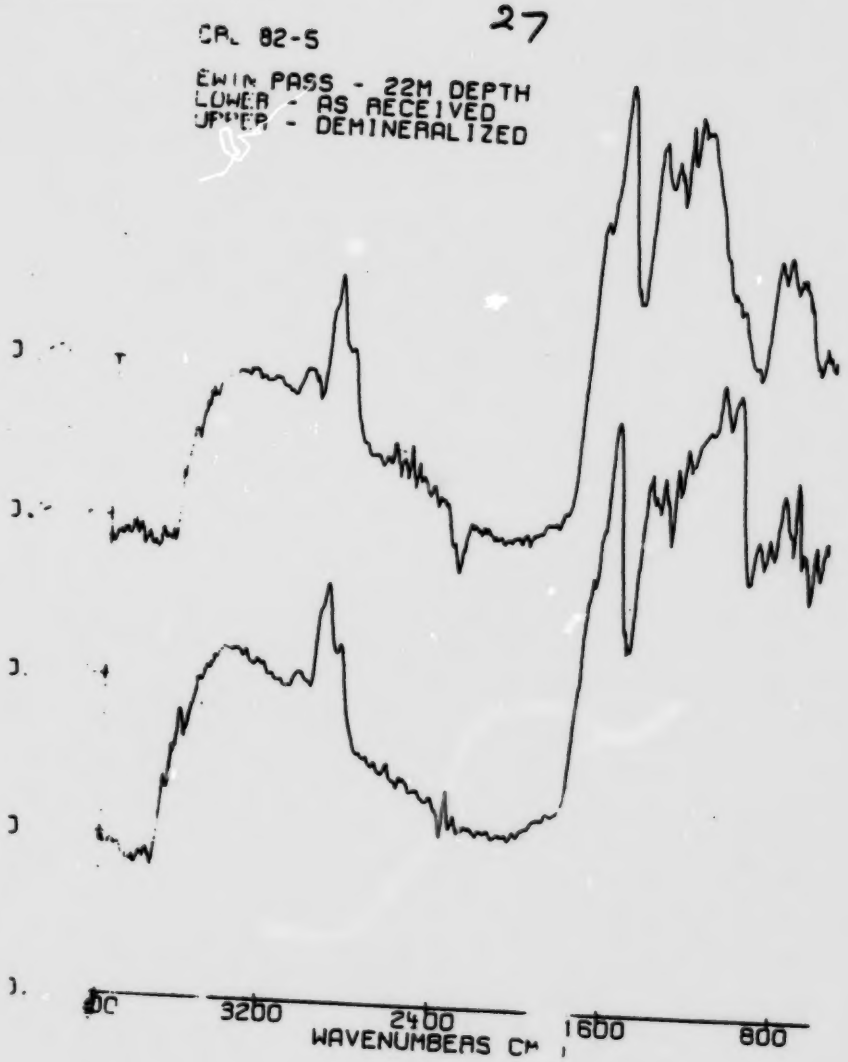

CRL 82-5
EWIN PASS - 22M DEPTH
LOWER - AS RECEIVED
UPPER - DEMINERALIZED
3200
2400
1600
800
WAVENUMBERS CM

FIGURE 13

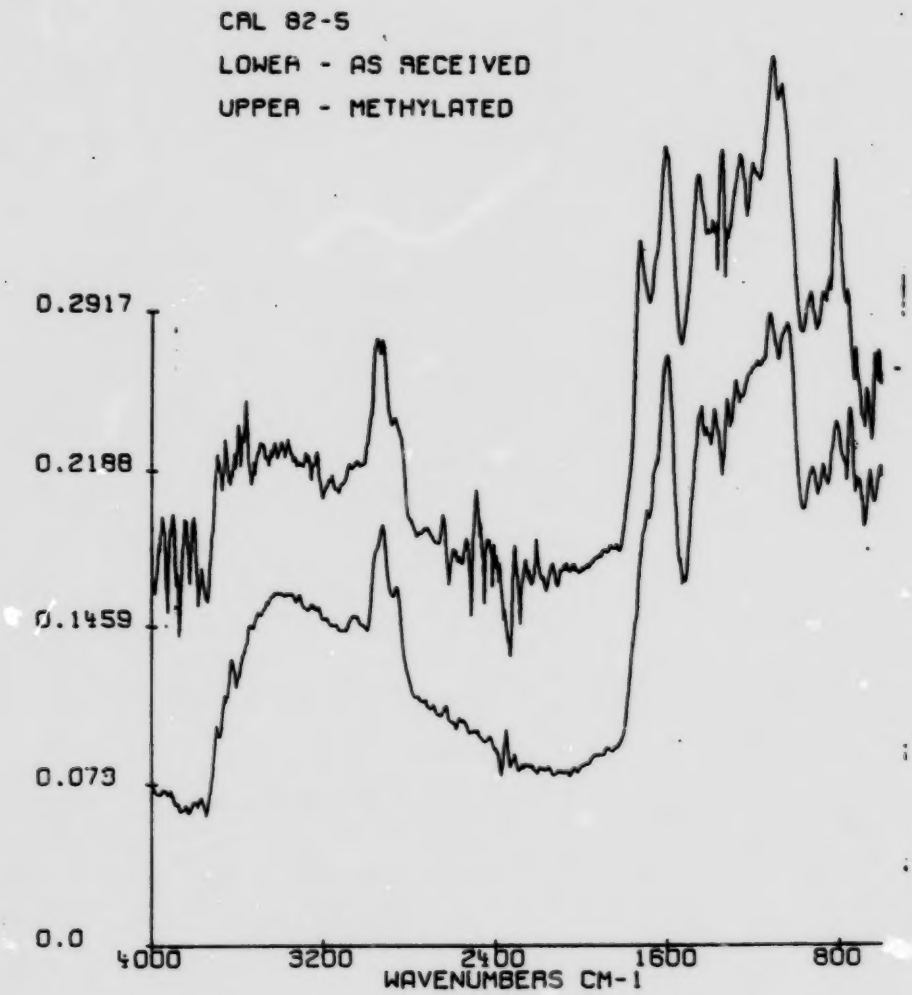

CAL 82-5
LOWER - AS RECEIVED
UPPER - METHYLATED
0.2917
0.2188
0.1459
0.073
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 14

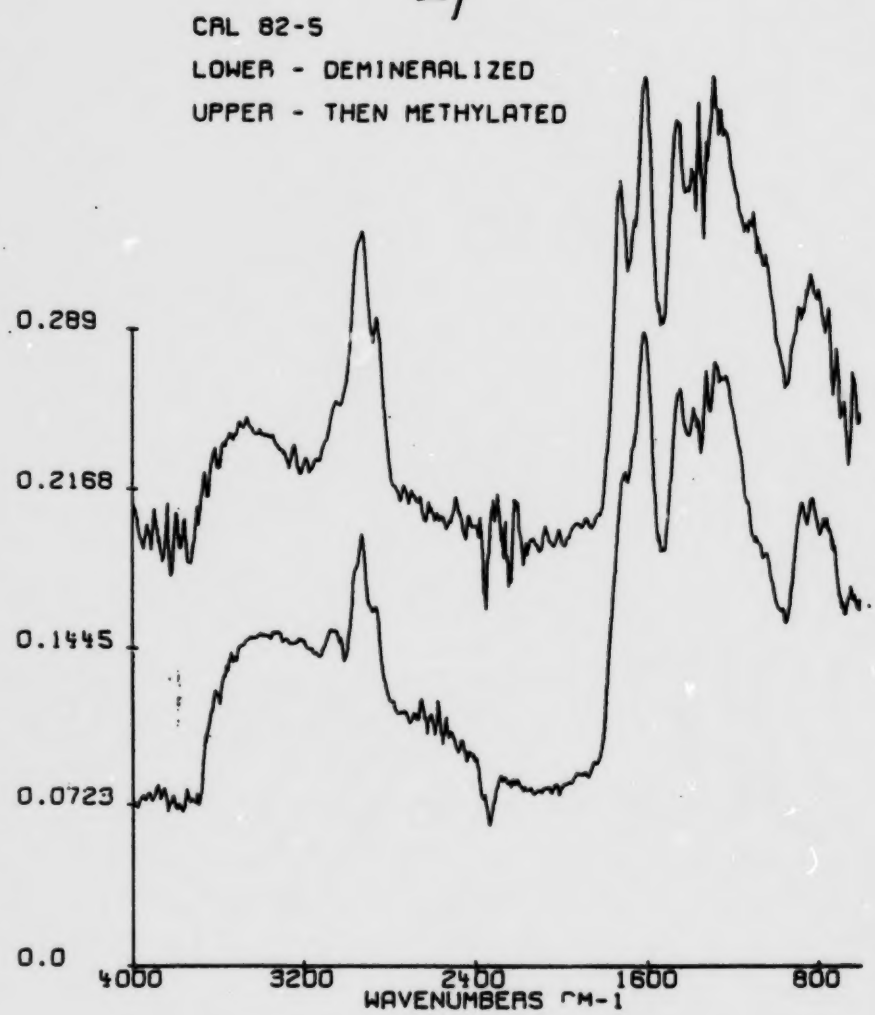

CAL 82-5
LOWER - DEMINERALIZED
UPPER - THEN METHYLATED
0.289
0.2168
0.1445
0.0723
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 15

CAL 82-6
SAMPLE CAL 82-1 OXIDIZED FOR 7 DAYS
AT CAL EDMONTON

LOWER SPECTRUM - AS RECEIVED
UPPER SPECTRUM - DEMINERALIZED

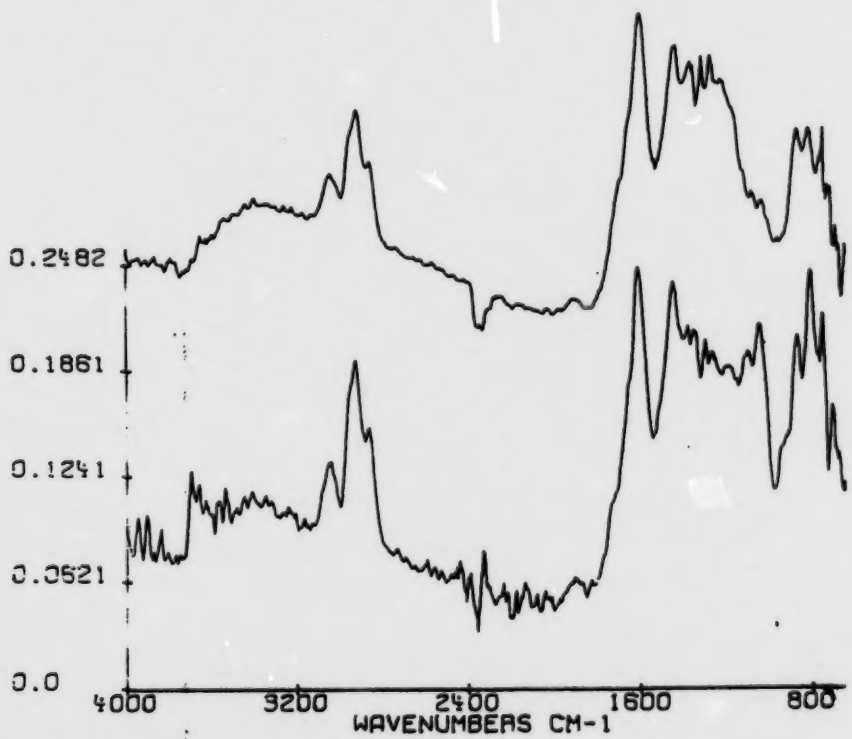


FIGURE 16

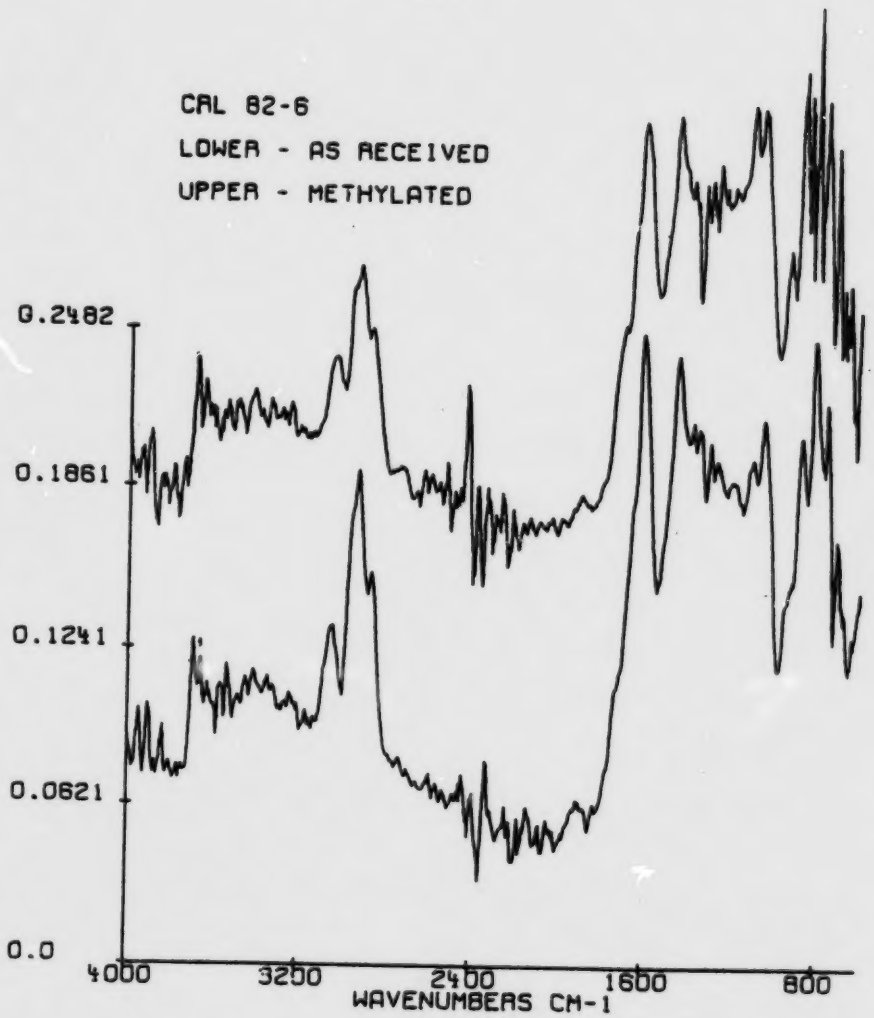

CAL 82-6
LOWER - AS RECEIVED
UPPER - METHYLATED
0.2482
0.1861
0.1241
0.0621
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 17

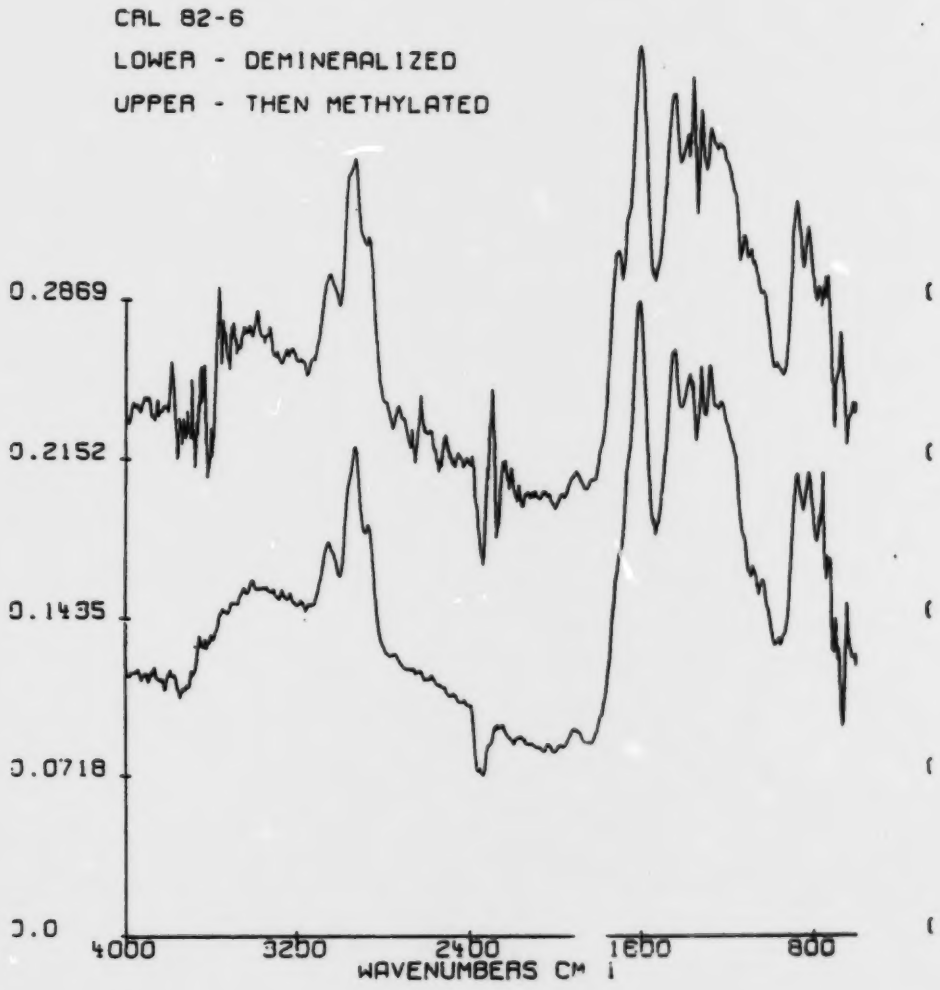

CAL 82-6
LOWER - DEMINERALIZED
UPPER - THEN METHYLATED
0.2869
0.2152
0.1435
0.0718
0.0
4000
3250
2400
1600
800
WAVENUMBERS CM -1

FIGURE 18

CAL 82-7
BRITISH PETROLEUM ADIT SAMPLE
LOWER SPECTRUM - AS RECEIVED
UPPER SPECTRUM - DEMINERALIZED

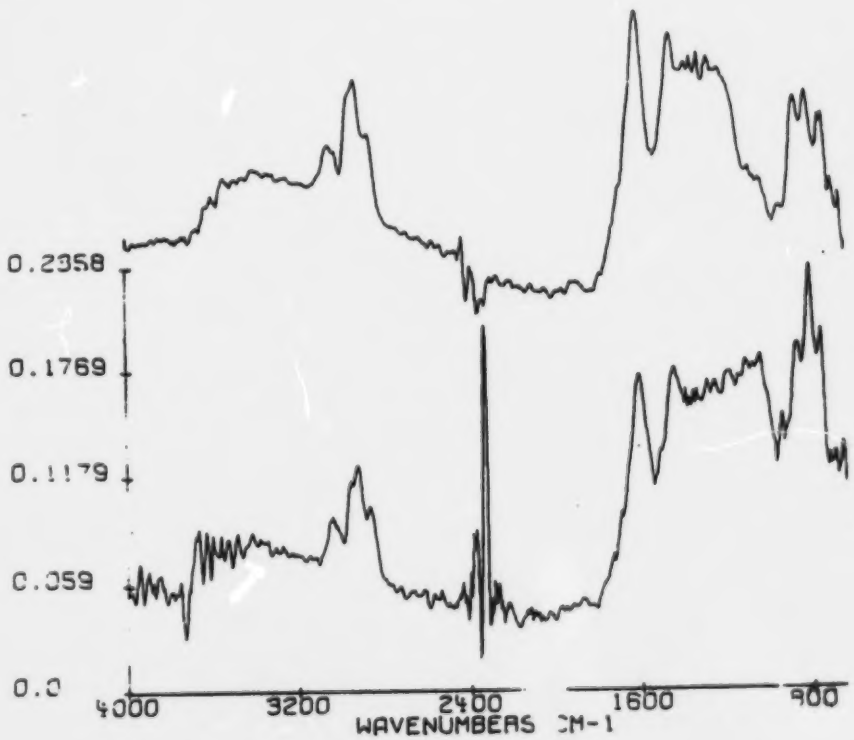


FIGURE 19

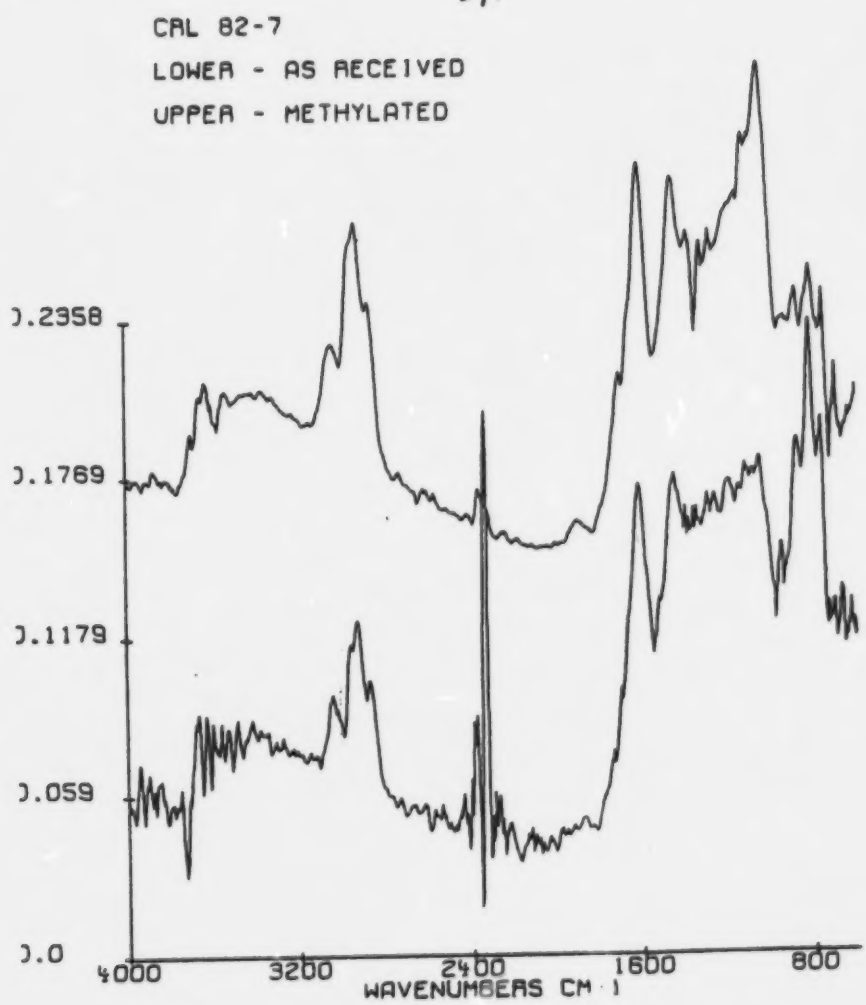

CAL 82-7
LOWER - AS RECEIVED
UPPER - METHYLATED
0.2358
0.1769
0.1179
0.059
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 20

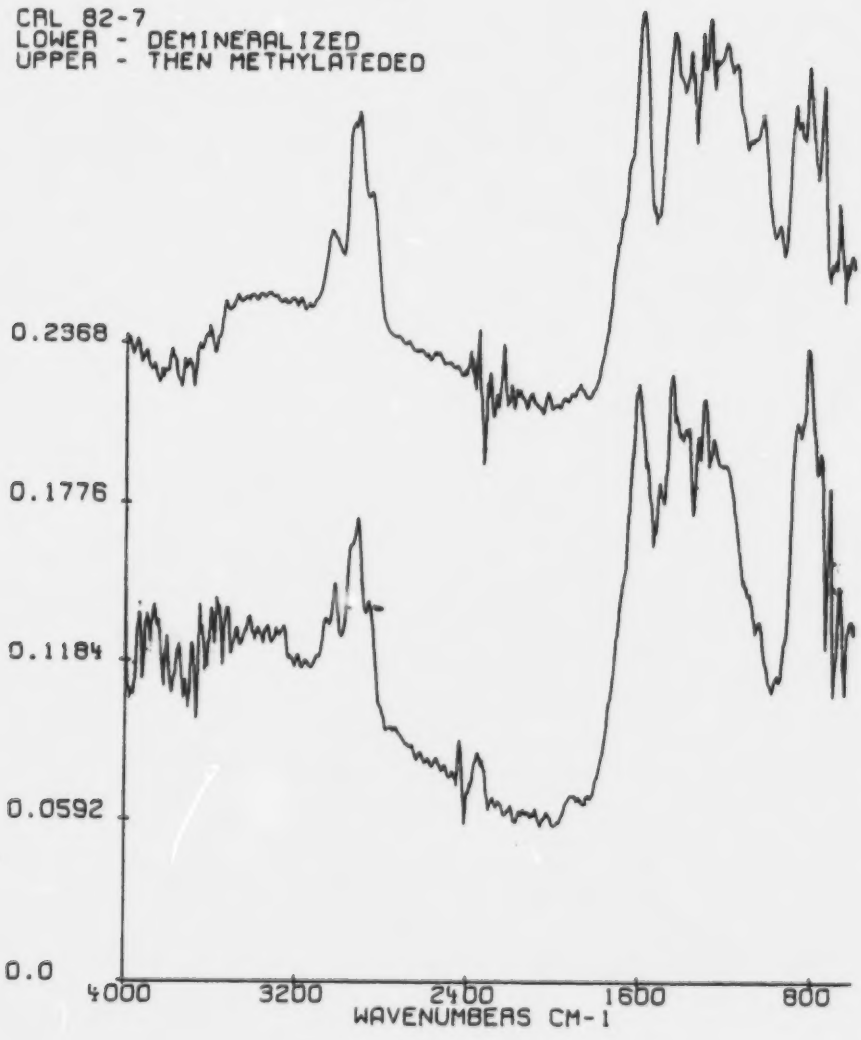

CAL 82-7
LOWER - DEMINERALIZED
UPPER - THEN METHYLATEDED
0.2368
0.1776
0.1184
0.0592
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 21

CRL 82-8 COLEMAN COLLIERIES
LOWER SPECTRUM - AS RECEIVED
UPPER SPECTRUM - DEMINERALIZED

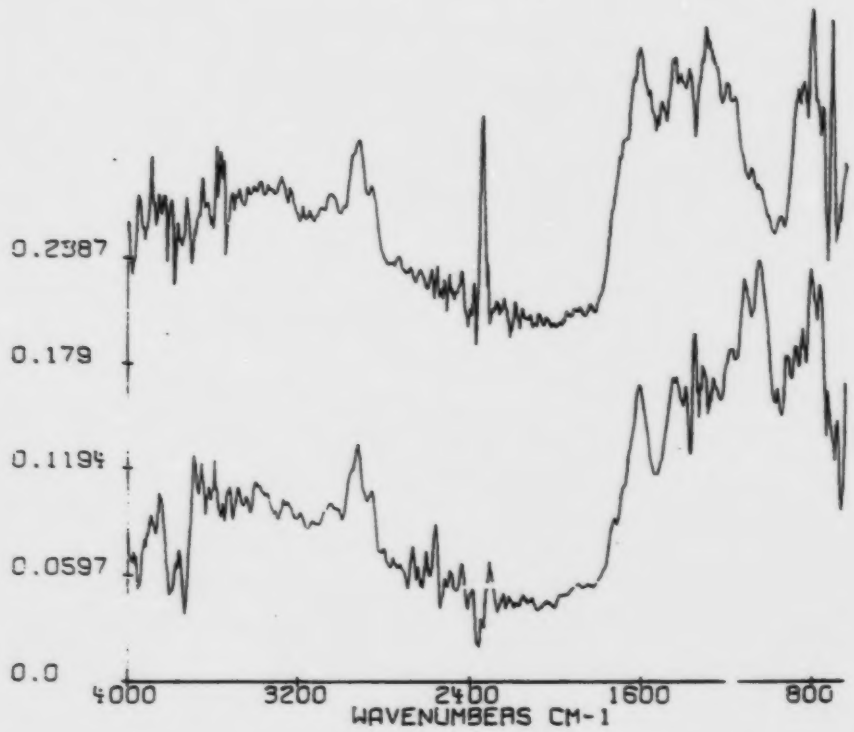


FIGURE 23

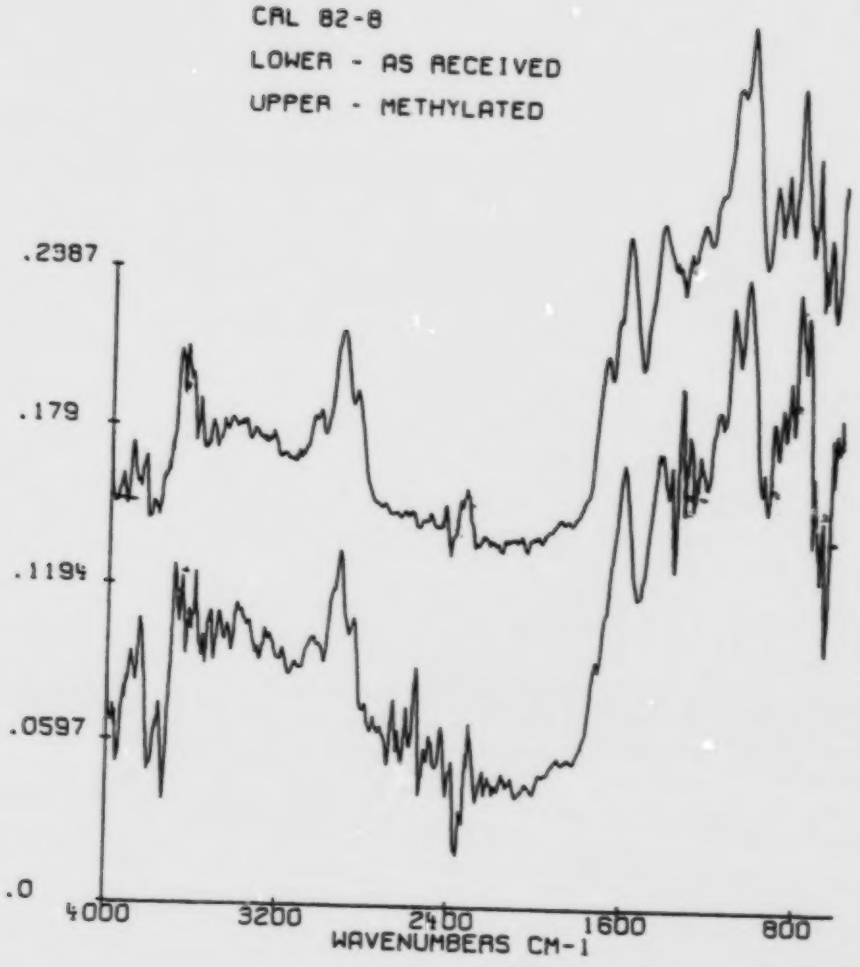

CAL 82-8
LOWER - AS RECEIVED
UPPER - METHYLATED
.2387
.179
.1194
.0597
.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 23

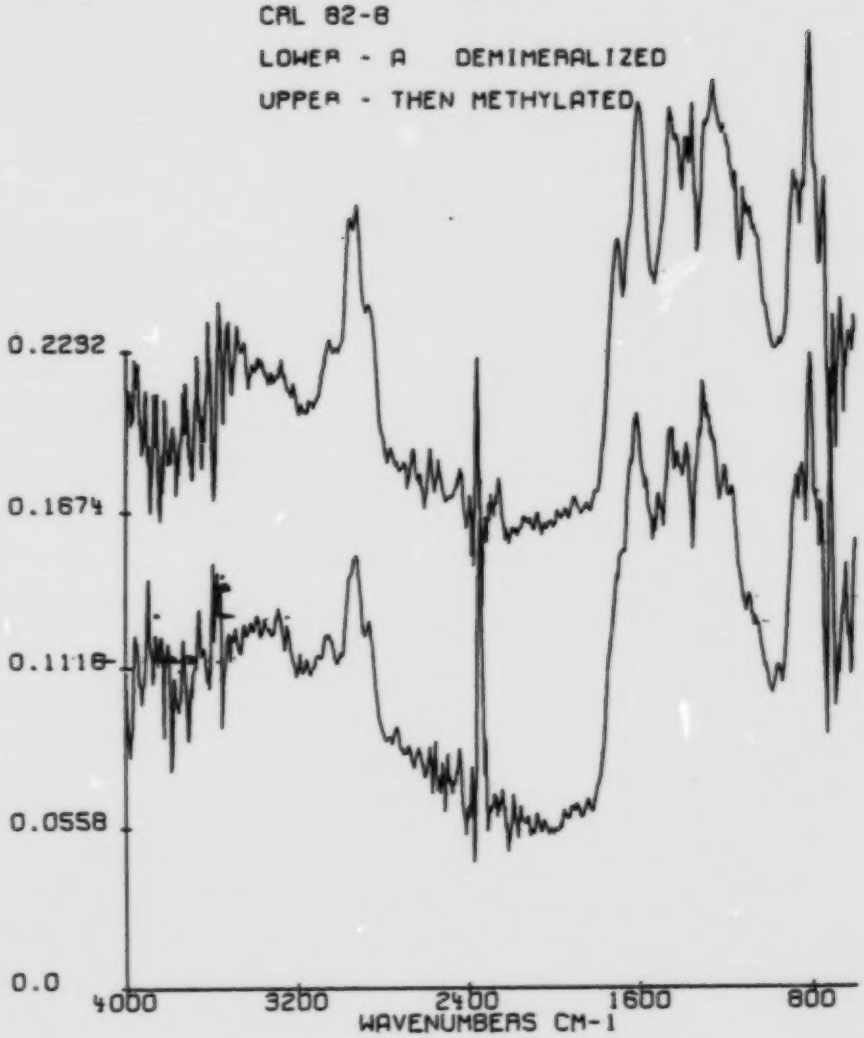

CAL 82-8
LOWER - A DEMINERALIZED
UPPER - THEN METHYLATED
0.2232
0.1674
0.1116
0.0558
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 24

CAL 82-9 JUDY CREEK.
CLEANED COAL
LOWER SPECTRUM - AS RECEIVED
UPPER SPECTRUM - DEMINERALIZED

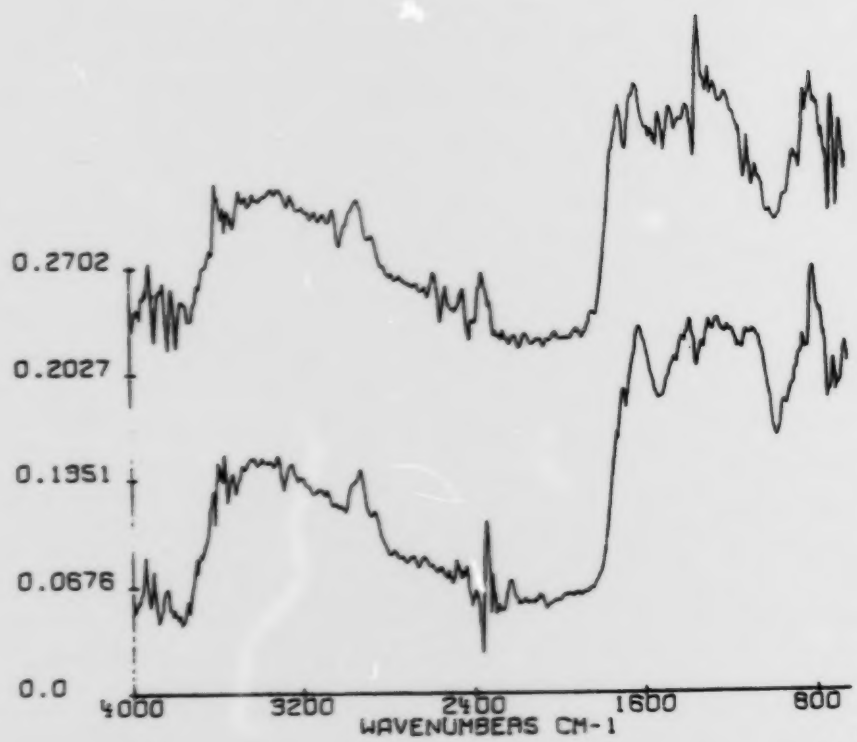


FIGURE 25

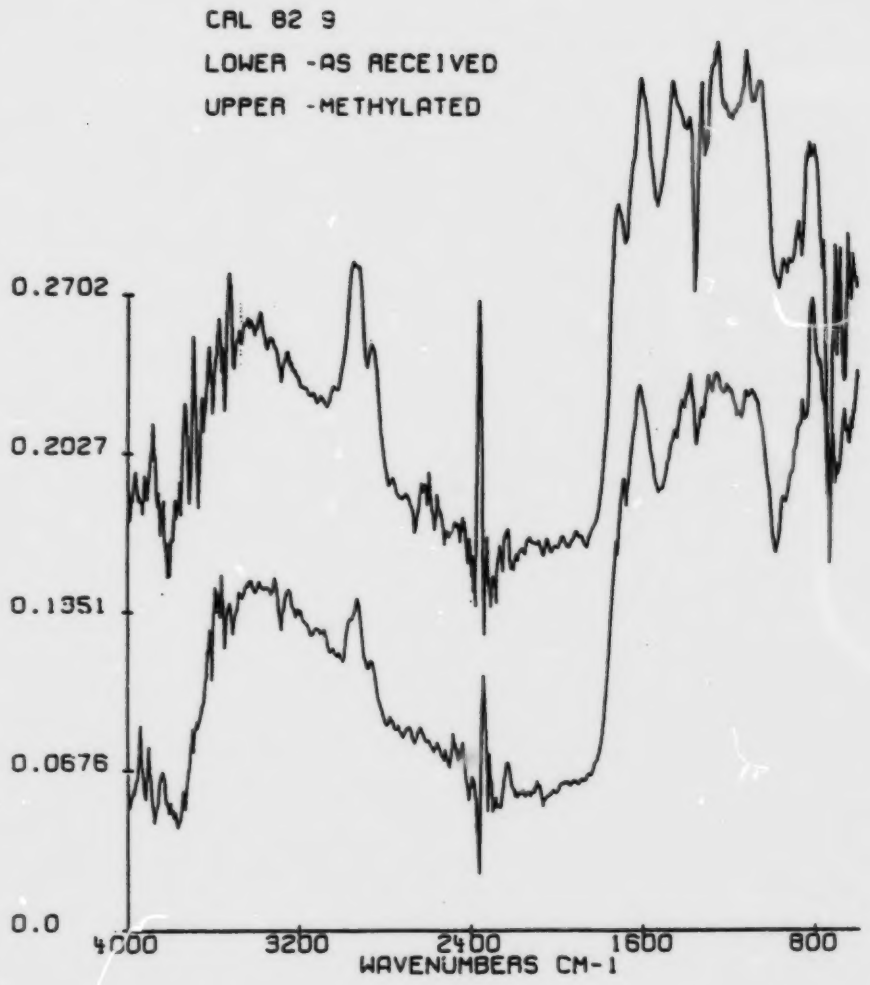

CAL 82 9
LOWER -AS RECEIVED
UPPER -METHYLATED
0.2702
0.2027
0.1351
0.0676
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 25

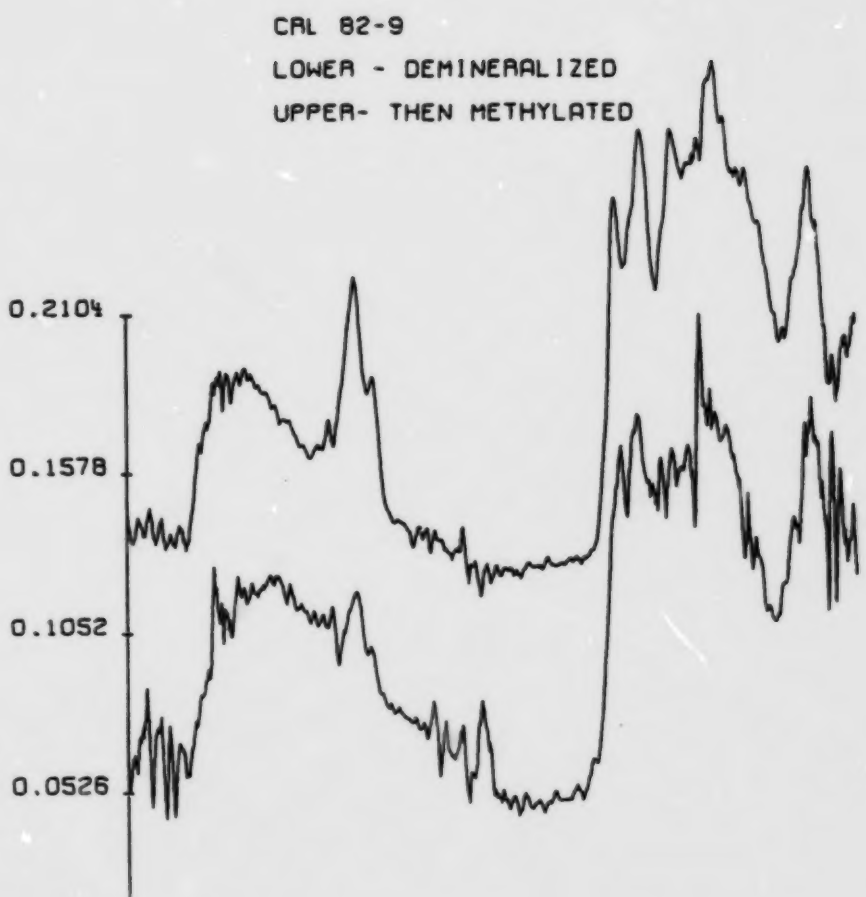

CAL 82-9
LOWER - DEMINERALIZED
UPPER- THEN METHYLATED
0.2104
0.1578
0.1052
0.0526
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 27

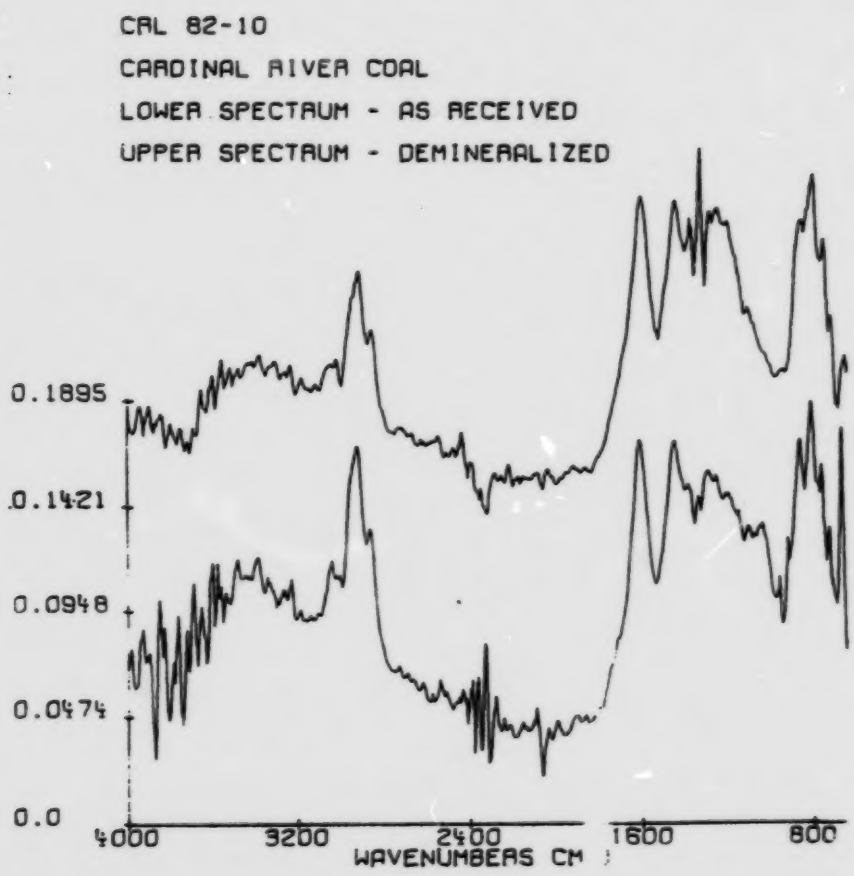

CRL 82-10
CARDINAL RIVER COAL
LOWER SPECTRUM - AS RECEIVED
UPPER SPECTRUM - DEMINERALIZED
0.1895
0.1421
0.0948
0.0474
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM

FIGURE 28

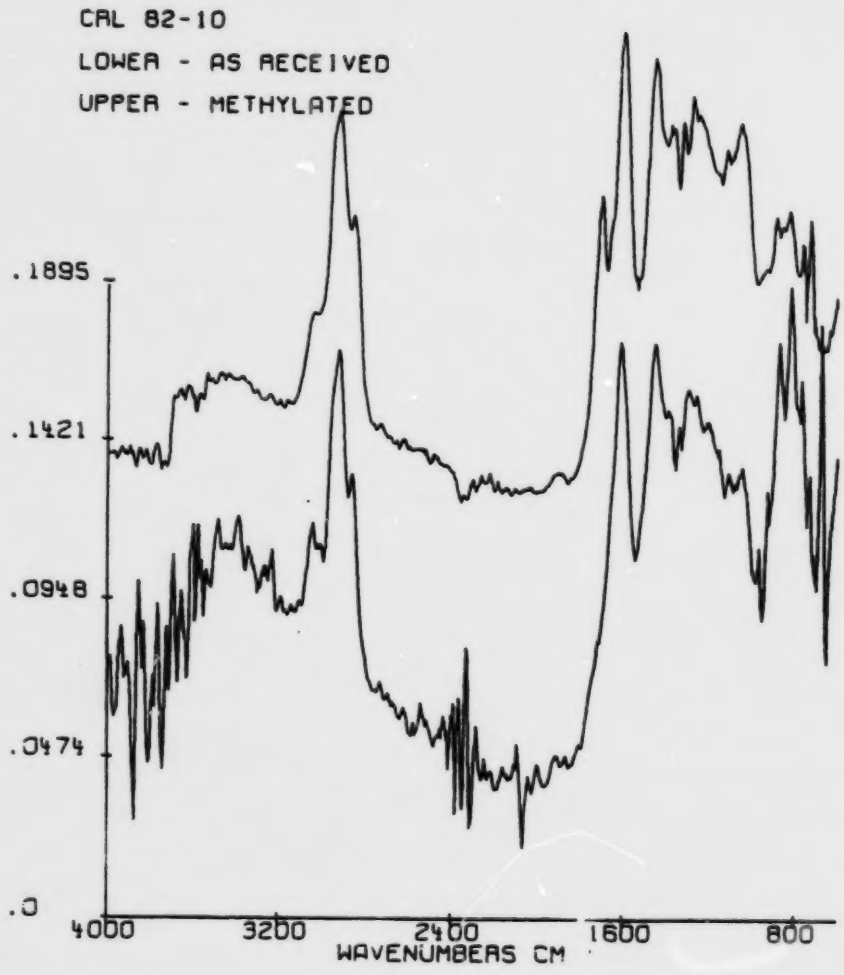

CAL 82-10
LOWER - AS RECEIVED
UPPER - METHYLATED
.1895
.1421
.0948
.0474
.0
4000
3200
2400
1600
800
WAVENUMBERS CM

FIGURE # 29

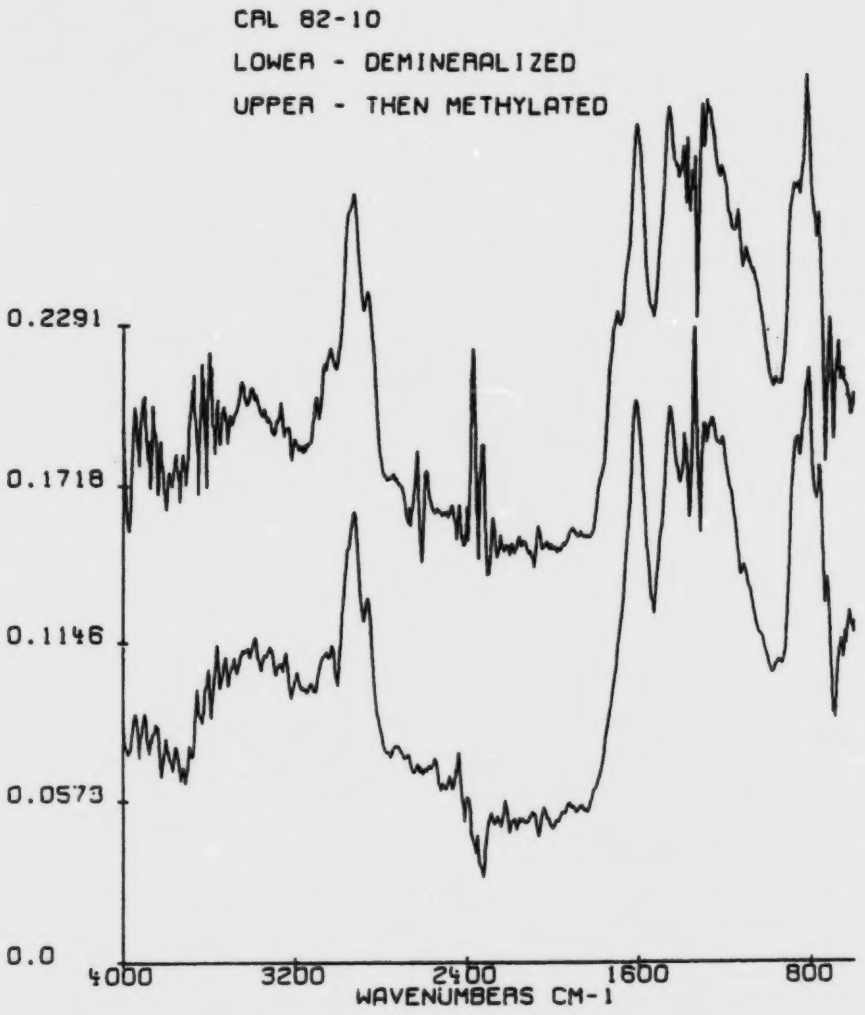

CAL 82-10
LOWER - DEMINERALIZED
UPPER - THEN METHYLATED
0.2291
0.1718
0.1146
0.0573
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 30

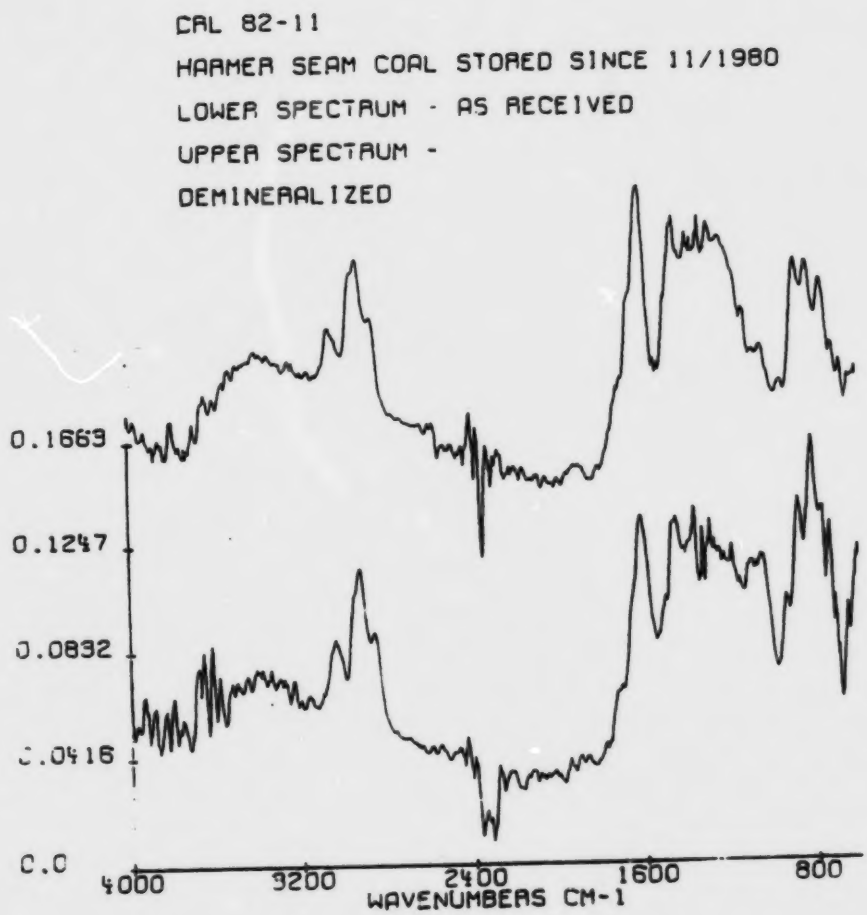

CAL 82-11
HARMER SEAM COAL STORED SINCE 11/1980
LOWER SPECTRUM - AS RECEIVED
UPPER SPECTRUM -
DEMINERALIZED
0.1663
0.1247
0.0832
0.0416
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 32

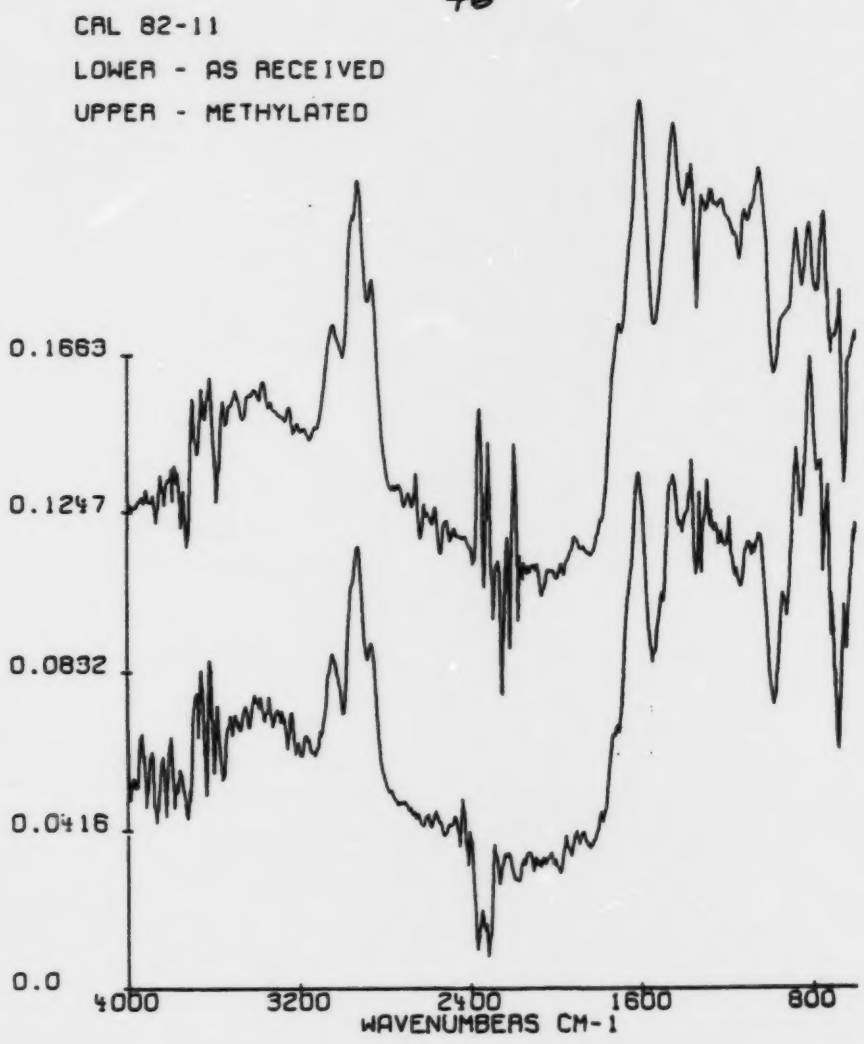

CAL 82-11
LOWER - AS RECEIVED
UPPER - METHYLATED
0.1663
0.1247
0.0832
0.0416
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 32

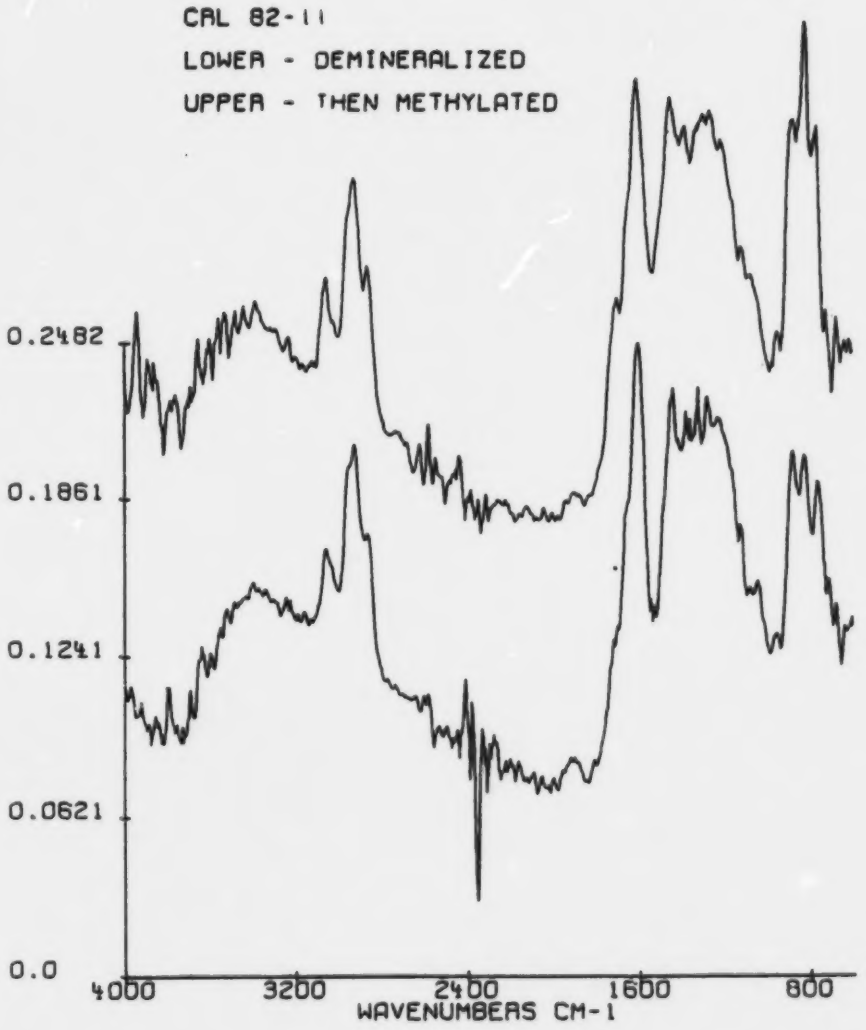

CAL 82-11
LOWER - DEMINERALIZED
UPPER - THEN METHYLATED
0.2482
0.1861
0.1241
0.0621
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 33

DRIFT SPECTRA OF KAOLINITE &
LOW-TEMPERATURE ASH SAMPLES FROM
CRL SERIES BITUMINOUS COALS

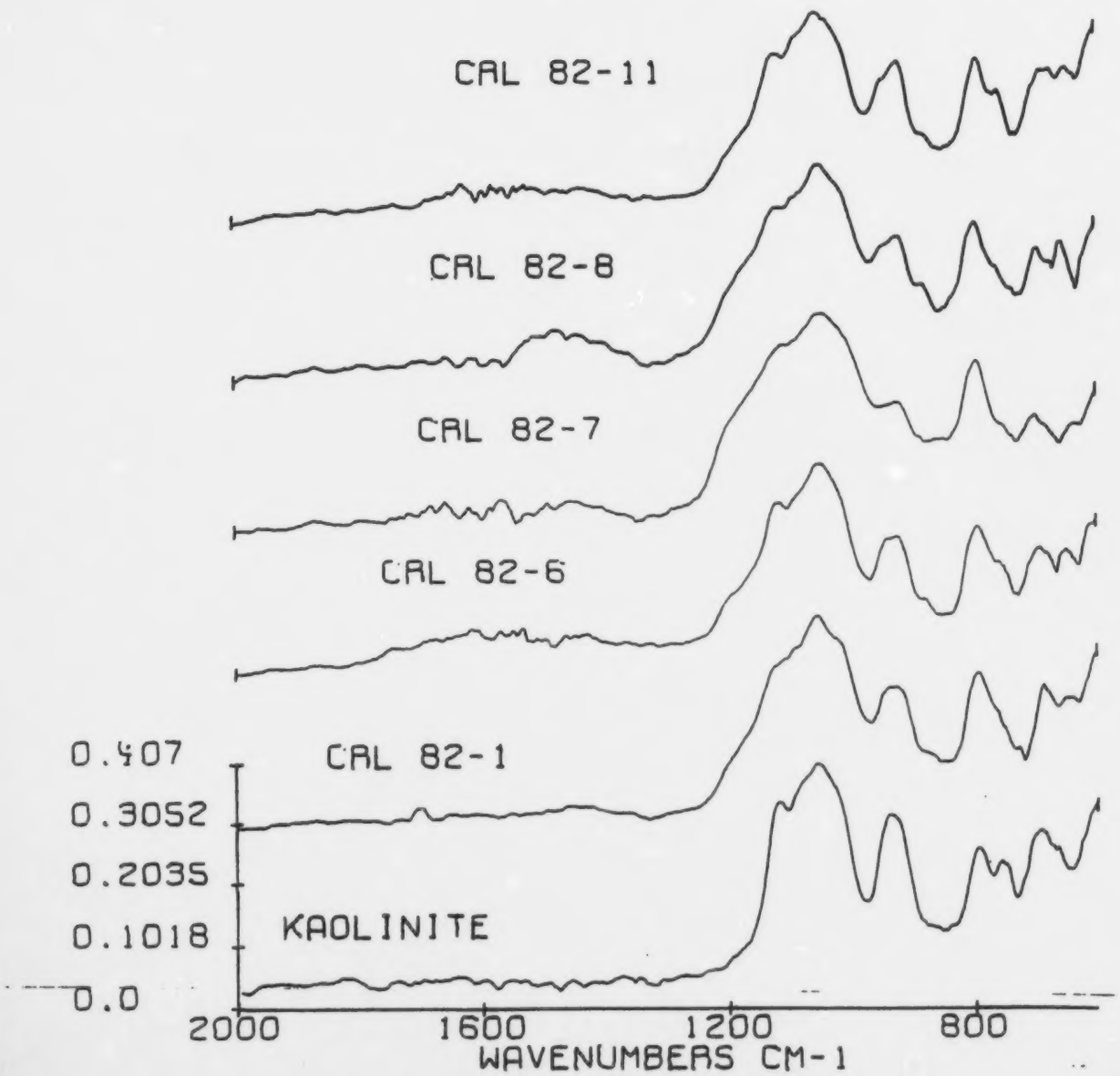


FIGURE 34

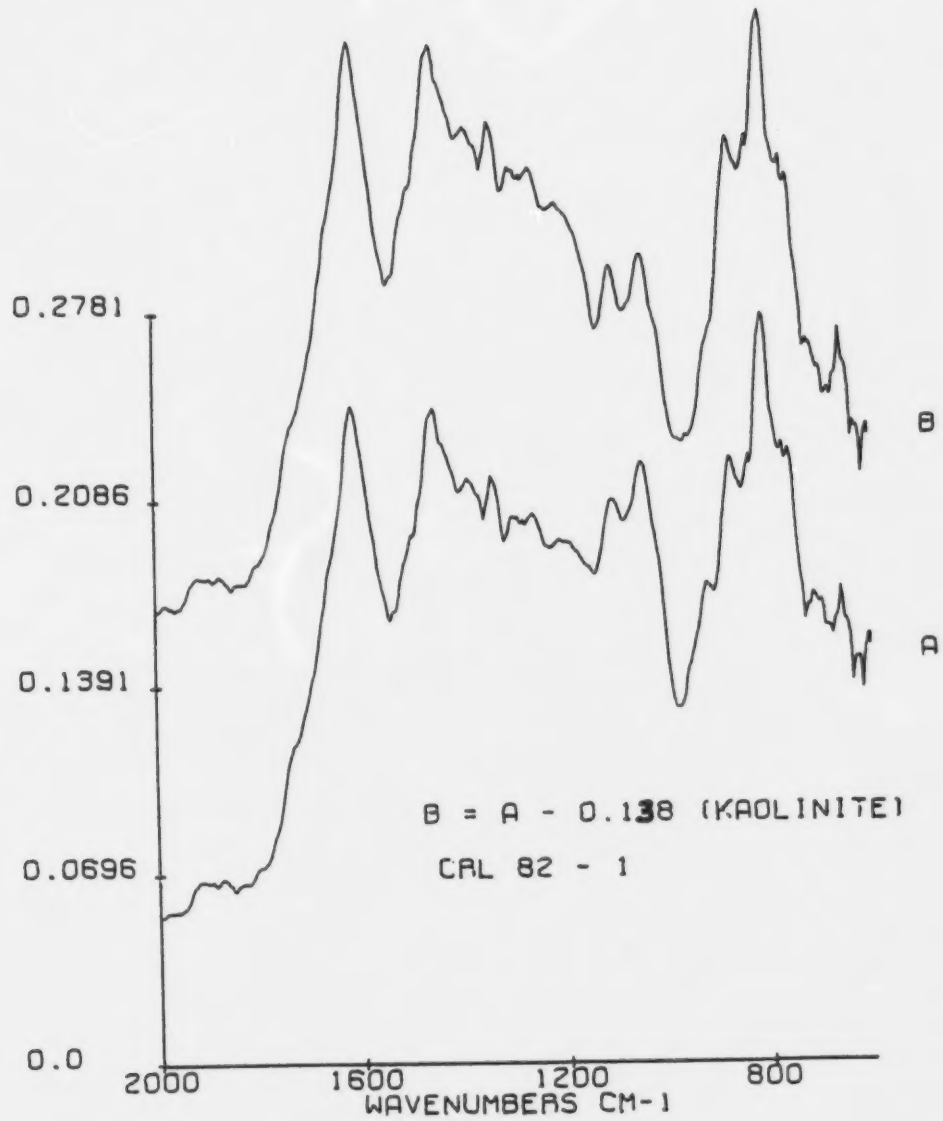

0.2781
0.2086
0.1391
0.0696
0.0
2000
1600
1200
800
WAVENUMBERS CM-1
B
A
B = A - 0.138 (KAOLINITE)
CAL 82 - 1

FIGURE 35

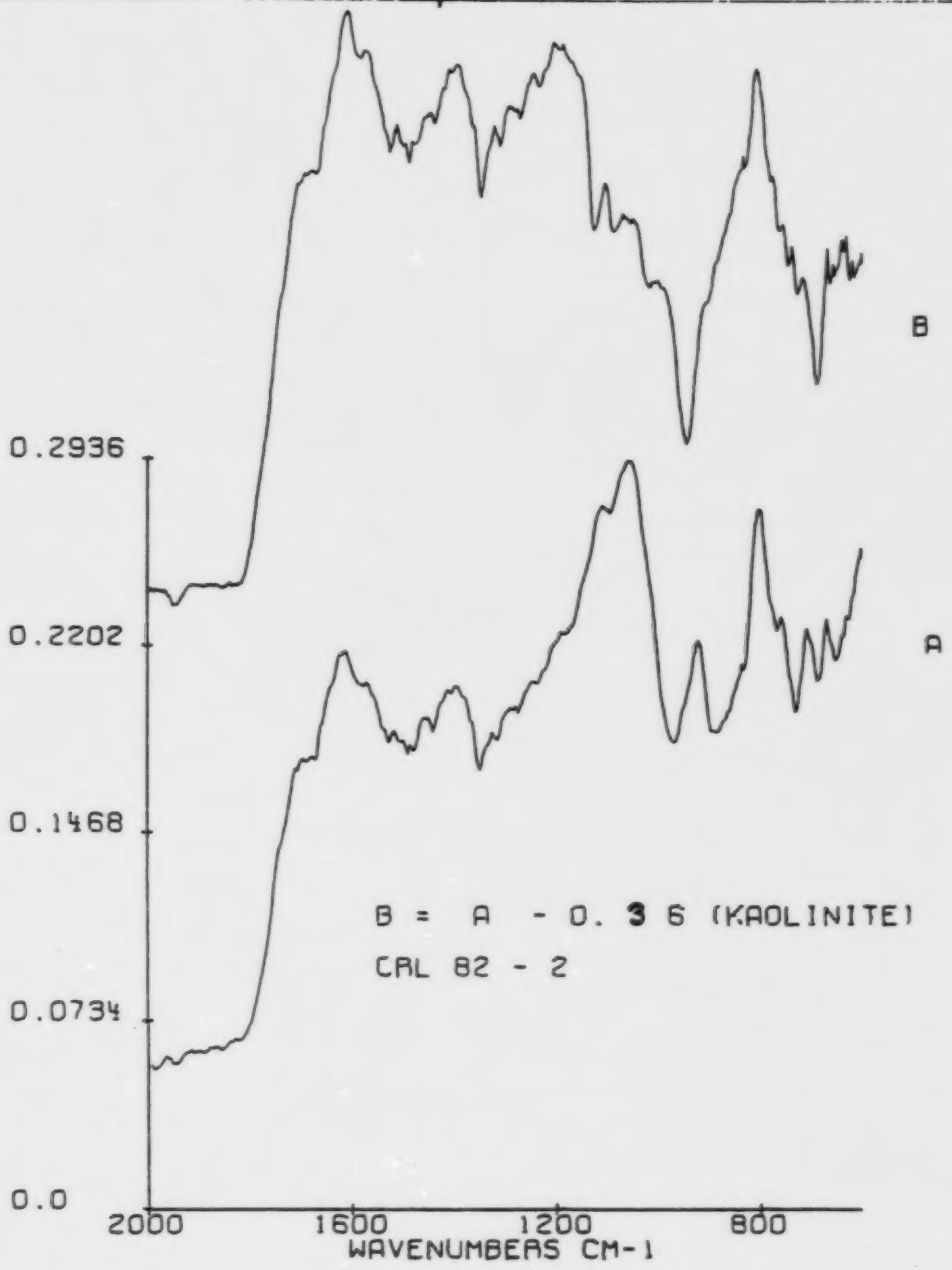

B
A
0.2936
0.2202
0.1468
0.0734
0.0
2000
1600
1200
800
WAVENUMBERS CM-1
B = A - 0.36 (KAOLINITE)
CRL 82 - 2

FIGURE 36

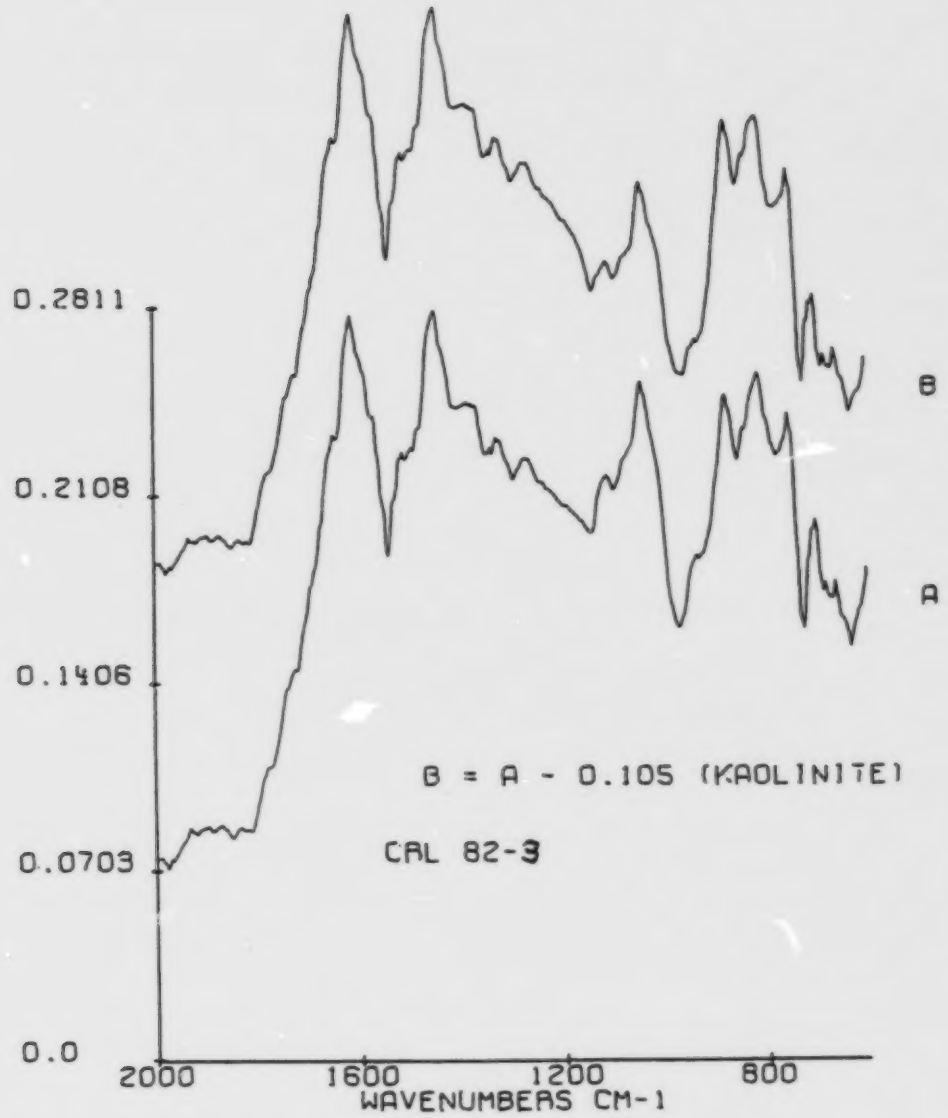

0.2811
0.2108
0.1406
0.0703
0.0
2000
1600
1200
800
WAVENUMBERS CM-1
B
A
B = A - 0.105 (KAOLINITE)
CRL 82-3

FIGURE 37

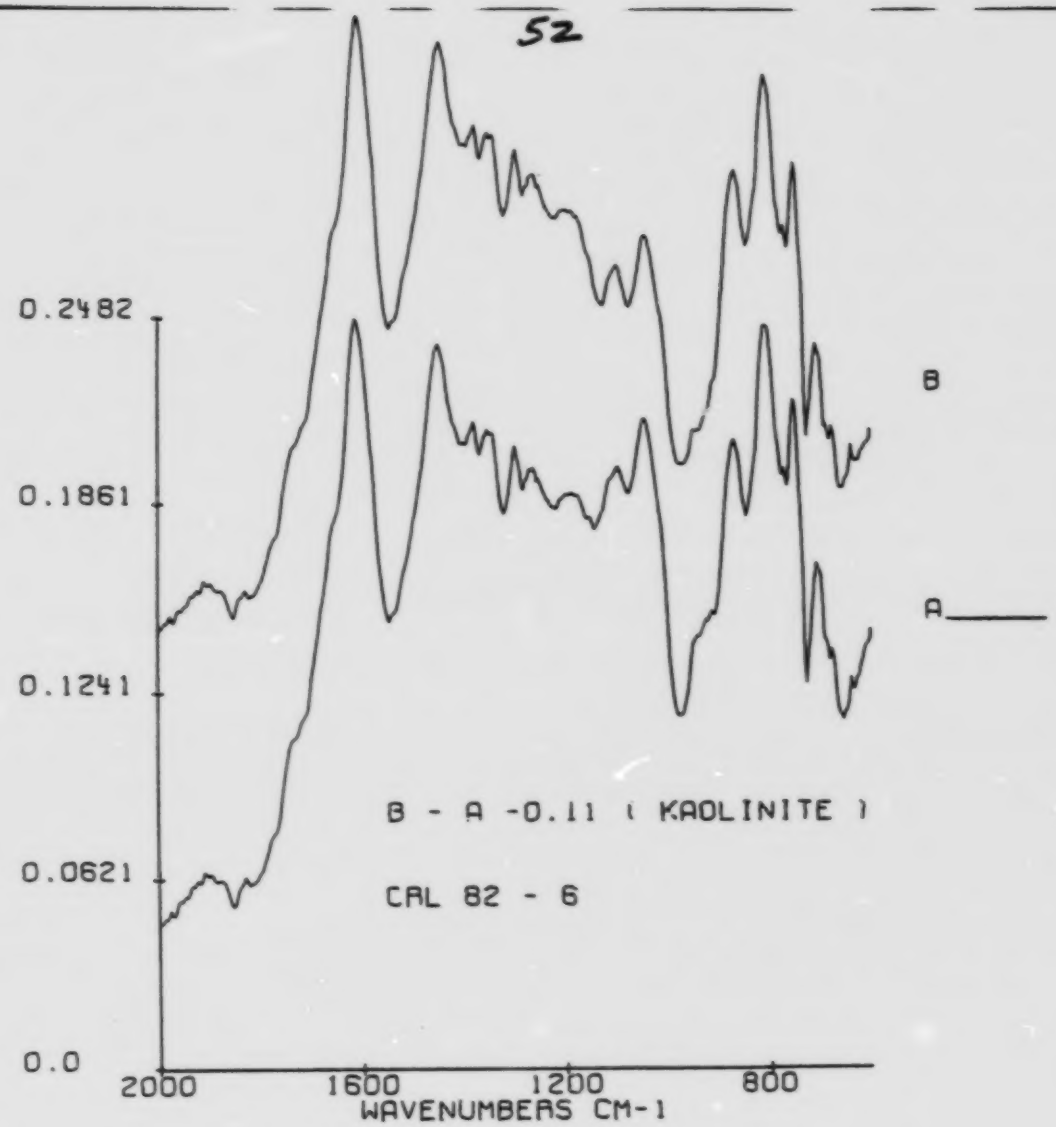

0.2482
0.1861
0.1241
0.0621
0.0
2000
1600
1200
800
WAVENUMBERS CM-1
B
A
B - A -0.11 (KAOLINITE)
CAL 82 - 6

FIGURE 38

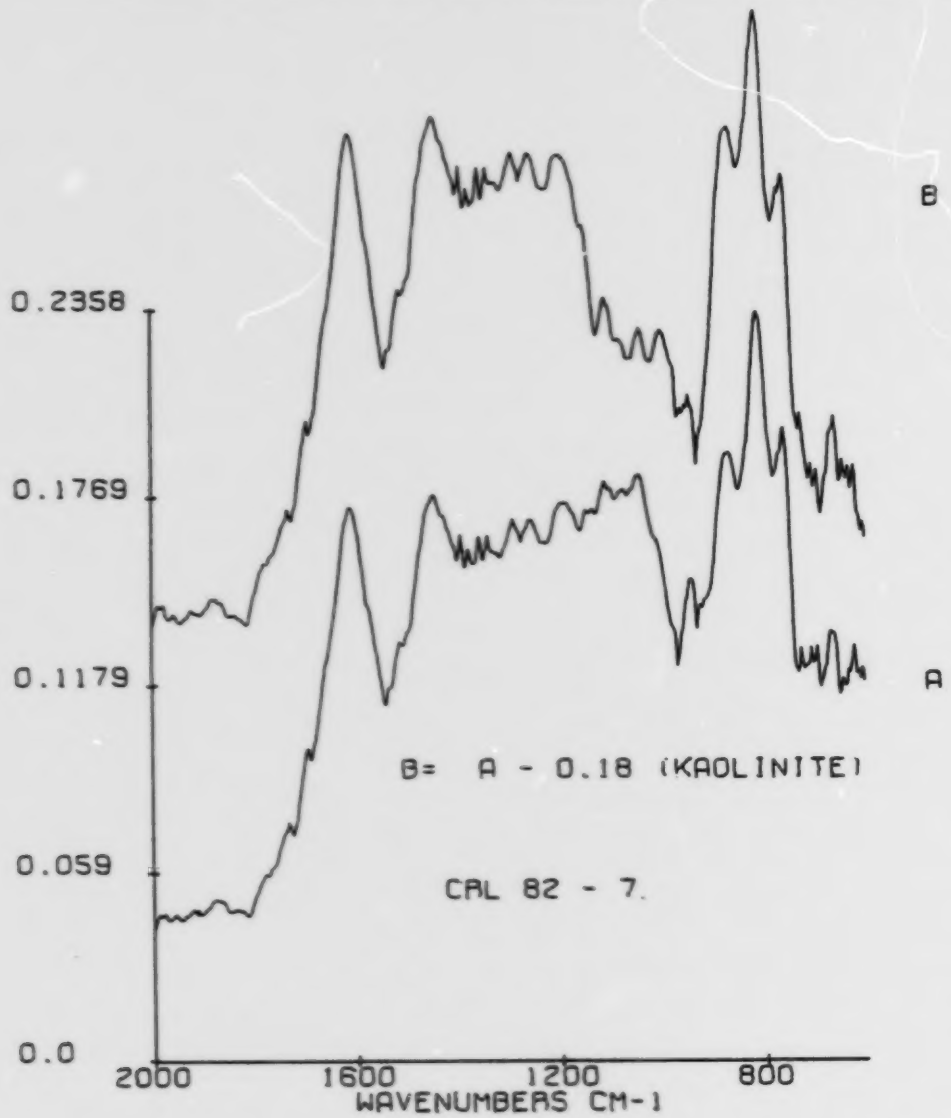

B
A
0.2358
0.1769
0.1179
0.059
0.0
B= A - 0.18 (KAOLINITE)
CAL 82 - 7.
2000
1600
1200
800
WAVENUMBERS CM-1

FIGURE 39

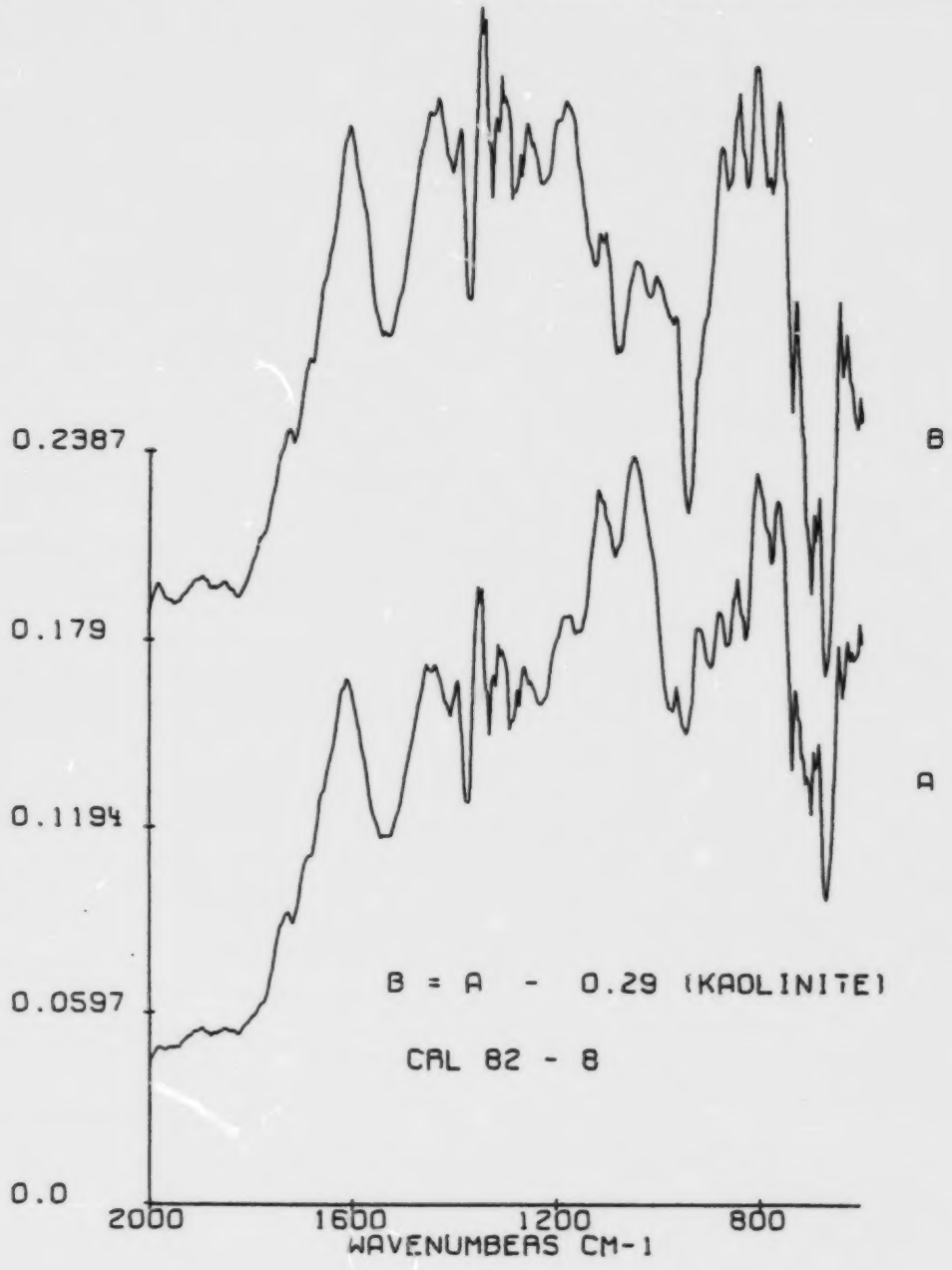

0.2387
0.179
0.1194
0.0597
0.0
B
A
B = A - 0.29 (KAOLINITE)
CAL 82 - 8
2000
1600
1200
800
WAVENUMBERS CM-1

FIGURE 40

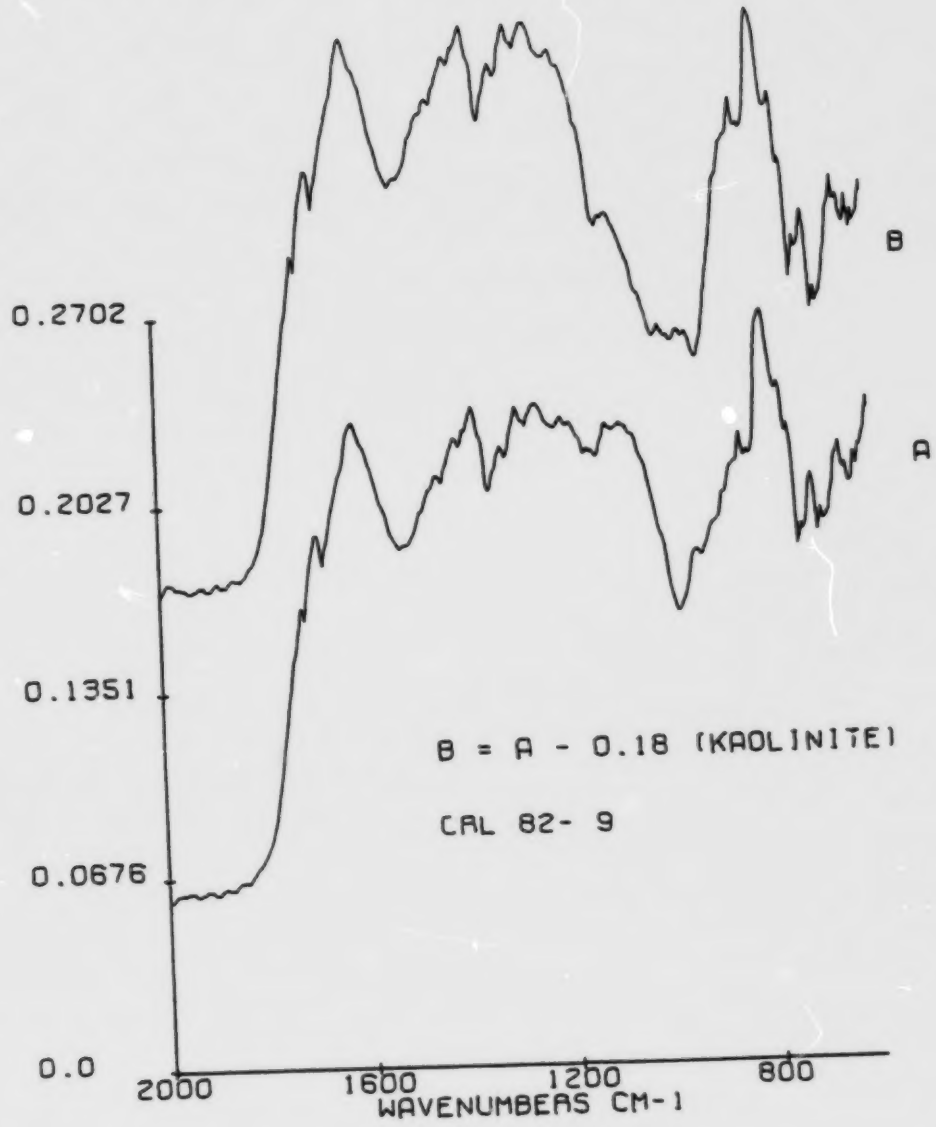

0.2702
0.2027
0.1351
0.0676
0.0
2000
1600
1200
800
WAVENUMBERS CM-1
B
A
B = A - 0.18 (KAOLINITE)
CAL 82- 9

FIGURE 41

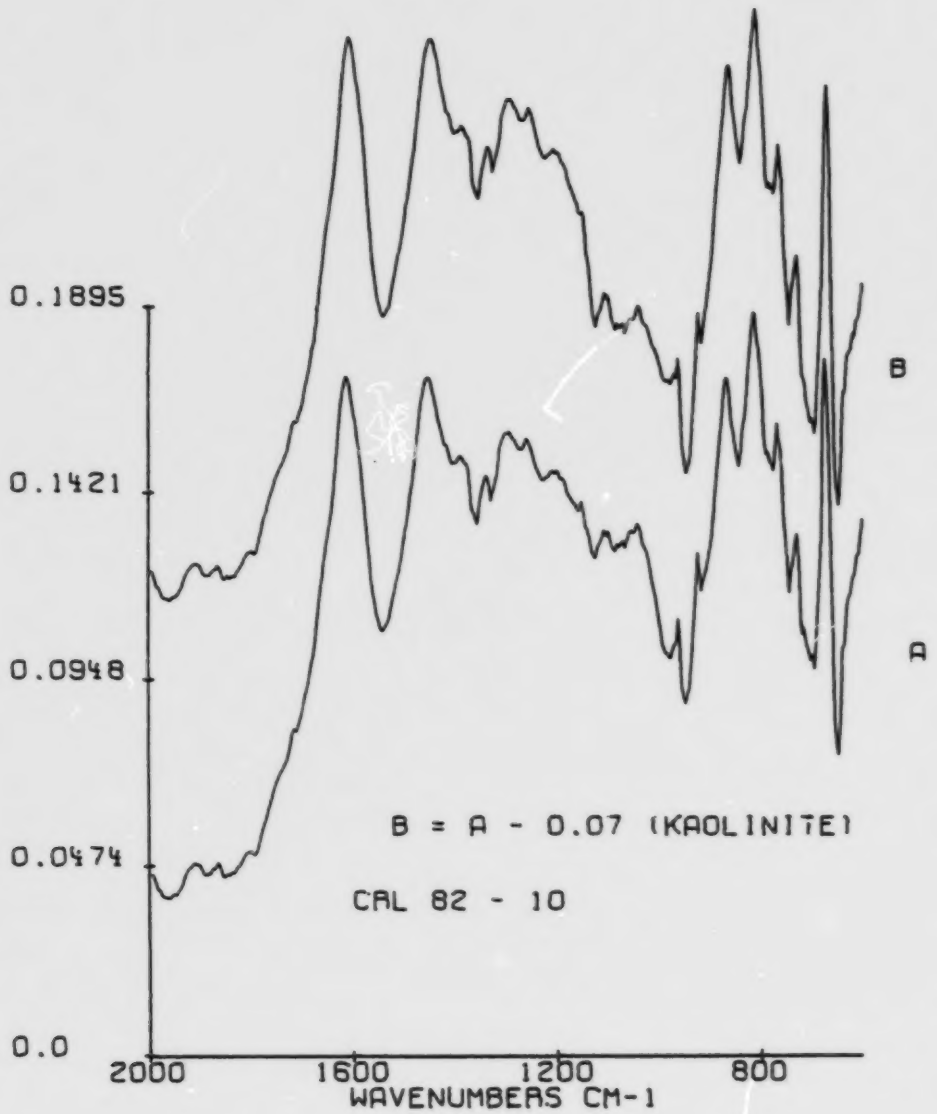

0.1895
0.1421
0.0948
0.0474
0.0
2000
1600
1200
800
WAVENUMBERS CM-1
B
A
B = A - 0.07 (KAOLINITE)
CAL 82 - 10

FIGURE 42

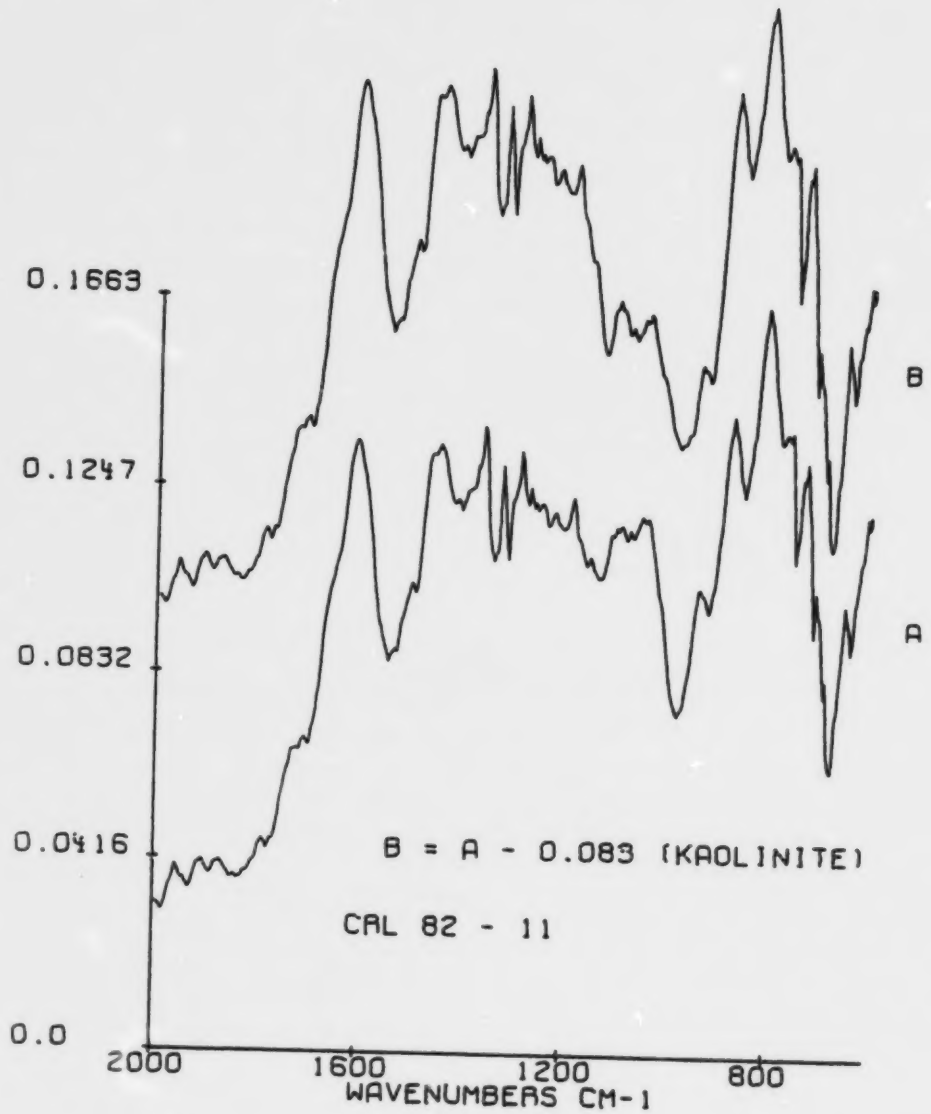

0.1663
0.1247
0.0832
0.0416
0.0
B
A
B = A - 0.083 (KAOLINITE)
CAL 82 - 11
2000
1600
1200
800
WAVENUMBERS CM-1

FIGURE 43

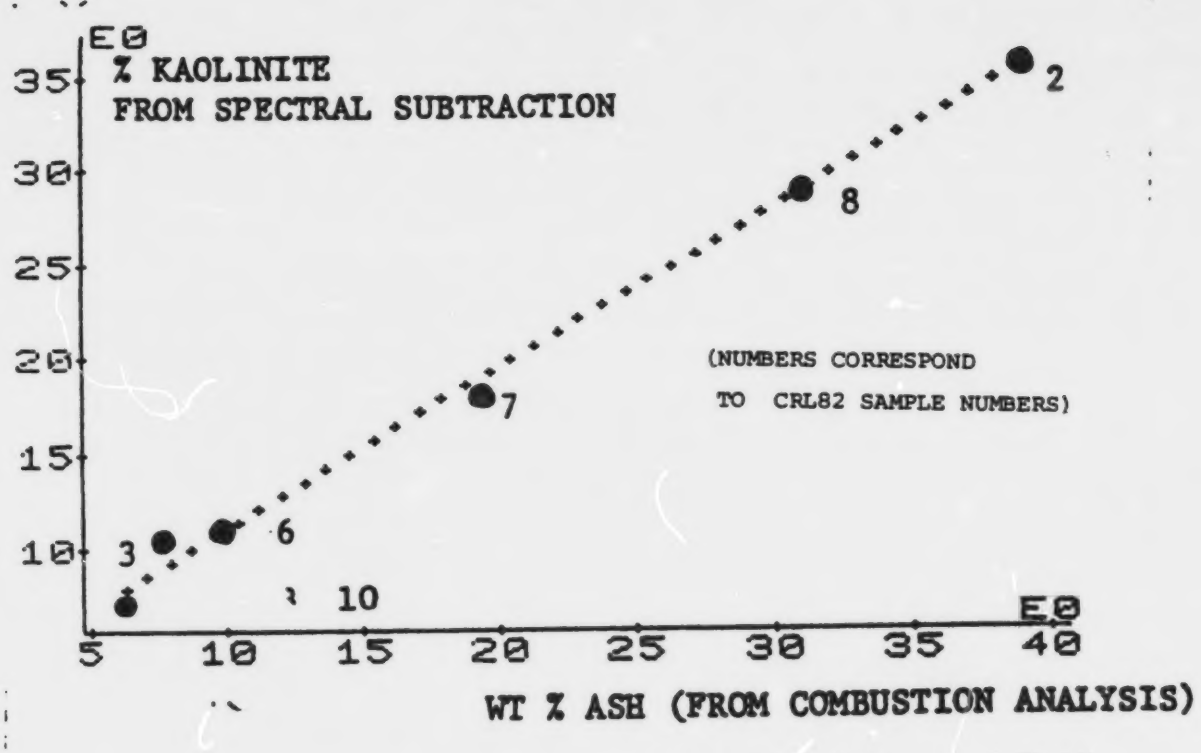

E0
% KAOLINITE
FROM SPECTRAL SUBTRACTION
35
30
25
20
15
10
2
8
7
6
3
10
(NUMBERS CORRESPOND
TO CRL82 SAMPLE NUMBERS)
E0
5
10
15
20
25
30
35
40
WT % ASH (FROM COMBUSTION ANALYSIS)

FIGURE 44

OXIDATION AND WEATHERING OF BITUMINOUS COALS
INTRODUCTION AND REVIEW OF PREVIOUS STUDIES USING INFRARED SPECTROSCOPY AND/OR CLASSICAL CHEMICAL ANALYSES

In this section of the report, a concise summary of previous work is presented, indicating a continuing lack of consensus about the added functionality in artificially oxidized or naturally weathered coals.

Previous studies have explored a variety of different coals, oxidized at a variety of different temperatures from ambient to approximately 200 degrees, and part of the lack of agreement on the nature of added oxygen may thus reflect coal-dependent and temperature-dependent phenomena.

Durie and his co-workers (1) reported in 1963 that oxidation of an Australian vitrain at 170 and at 190 degrees led eventually to the virtual disappearance of aliphatic structures and the appearance of aromatic carboxylic acid groups. At earlier stages of oxidation, Painter and his co-workers (2) concluded that oxidation of PSOC-337 bituminous coal at 150 degrees generates carboxylate (-CO2-) and carbonyl (probably aryl alkyl ketonic) groups at the expense of methylene groups, while Bouwman and Freriks (3) concluded from an FTIR study of samples from a coal storage pile which had undergone spontaneous heating that carboxylic acid groups were generated.

Albers, Lenart, and Oerlert (4) suggested that increases in carbonyl content (assumed quinonoid) and in non-reactive oxygen (with little change in hydroxyl groups) occurred on oxidation of two bituminous coals at 129 and at 148 degrees.

In recently reported work, Liotta and his colleagues (5,6) have claimed that ether linkages are generated from ambient-temperature weathering of Illinois No. 6 bituminous coal.

DeVries, Bokhoven, and Dormans (7) found that wet analytical techniques indicated increases in acidic hydroxyl, carboxylic acid, and ketonic groups accompanying oxidations of two bituminous coals at 100 degrees. Berkowitz and his colleagues (8) report that aerial oxidation of Western Canadian bituminous coals generates ketonic forms, with virtually no increase in acidic oxygen-containing groups. Nandi, Montgomery, and their co-workers (9) reported that the carbonyl (ketone or quinone) of Balmer 10 low-volatile bituminous coal is unchanged after oxidation at 100 degrees for 3 days, and no carboxylic acidity is detectable, although the brief oxidation eliminates the swelling properties of the coal. It was suggested that the small amount of additional oxygen was in the form of crosslinking ether groups.

In the past year, other studies of coal oxidation at between 150 and 300 degrees have been published (Griffiths and co-workers (10), Fuller and Smyrl (11)) using diffuse reflectance infrared Fourier Transform (D R I F T) spectroscopy. Their results are in concordance with the early work by Durie and co-workers (1); the major additional pieces of information are assignments of high-frequency carbonyl infrared absorptions to carboxylic acid anhydride and/or aryl carbonate functions.

More recently, Lin and his colleagues (12) were unable to detect (via DRIFT spectroscopy) the development of carbonyl absorptions at the expense of aliphatic bands until artificial oxidation was quite extensive.

In the most recent communication on FTIR studies of coal, Tooke and Grint (13) have examined coals oxidized in the temperature range 125-325 degrees C, and they have ascribed peaks at 1680 cm.-1 in supposedly unoxidized coal to aromatic aldehyde functions. They have attempted self-deconvolution of the difference spectra at varying oxidation temperatures, but the major features represented therein reflect differing portions of water vapor in the KBr pellets used for sample dispersion.

Although the experimental conditions in many of these studies differ, it should be noted that even for apparently similar experiments with different coals, important experimental variables (such as the degree of subdivision of the coal, the flow rate of the oxidizing air, the extent of access of the coal to air) were often not controlled or were not specified.

A significant criticism of the proposals concerning the nature of increased oxygen functionality in the artificial oxidation experiments is that they are excessively simplistic. Surely, the complex nature of coal, with the presence of differing types of polycyclic aromatic and hydroaromatic ring systems bearing differing proportions of hydroxy or ether linkages, with interconnection (and possible cross-linking) of ring systems by aliphatic chains of variable lengths, is likely to yield a variety of added oxygen functionalities.

Further, although some postulates (9,11) account for changes in the properties of coals accompanying oxidation in terms of added cross-linking, these neglect the realities that the coals are rigid structures at the experimental temperatures, and cross-linking reactions involving significant motion within such structures (such as dehydrative condensation of adjacent phenolic moieties to form diaryl ethers, or successive hydrogen-abstraction and radical recombination reactions to yield aralkyl ethers) should be regarded sceptically in the absence of conclusive experimental support.

REFERENCES

1. R. B. Conrow, R. A. Durie, J. S. Shannon, and S. Sternhell, Fuel, 42, 275 (1963).

2. P. C. Painter, M. M. Coleman, R. W. Snyder, O. Mahajan, M. Komatsu, and P. L. Walker, Applied Spectroscopy, 35, 106 (1981).

3. R. Bouwman and I. L. C. Freriks, Fuel, 59, 315 (1980).

4. G. Albers, L. Lenart, and H. Oerlert, Fuel, 53, 47 (1974).

5. R. Liotta, G. Brons, and J. Isaacs, Abstract A27, pp. 157-162. International Conference on Coal Science, Dusseldorf, September 1981.

6. R. Liotta, G. Brons, and J. Isaacs, Fuel, 62, 781 (1983).

7. H. A. W. DeVries, C. Bokhoven, and H. N. M. Dormans, Brennstoff-Chemie, 50, 289 (1969).

8. N. Berkowitz, J. F. Fryer, B. S. Ignasiak, and A. J. Szladow, Fuel, 53, 141 (1974).

9. H. M. Wachowska, B. N. Nandi, and D. S. Montgomery, Fuel, 53, 212 (1974).

10. P. R. Griffiths, S. Wang, I. M. Hamadeh, P. W. Yang and D. E. Henry, Preprints, Division of Fuel Chemistry, American Chemical Society, Vol. 28, No. 1, p. 27 (1983).

11. E. L. Fuller, Jr., Editor. Coal and Coal products: Analytical Characterization Techniques. ACS Symposium Series, No. 205, p. 133 (1983).

12. M. C. Lin, F. E. Huggins, G. P. Huffman, and D. E. Lowenhaut, Abstract FUEL53, 186th American Chemical Society National Meeting, Washington, D.C., U.S.A., August 1983.

13. P. B. Tooke and A. Grint, Fuel, 62, 1003 (1983).

PROPOSED MECHANISMS OF AERIAL OXIDATION OF COALS BASED UPON PAIFT STUDIES OF DERIVATIZED COALS

A PRIORI, the rate of oxidation of a coal will be primarily dependent upon the following:

A. Chemical factors:

1. the ratio of aliphatic carbon alpha to aromatic rings to the total carbon;
2. the proportion of hydroxy-substitution present on aromatic rings;
3. the degree and distribution of ring condensation of the aromatic rings;
4. the average chain length and distribution about the average for aliphatically linked carbon.

B. Physical factors

1. Temperature;
2. Degree of subdivision of the coal;
3. Flow rate of oxidizing species;
4. Nature of oxidizing species (air or oxygen, dry or moist).

If we regard a prototypical coal as having the idealized structure of

Ar.(CH2)n.Ar

then the most probable sites of radical formation are adjacent to the aromatic rings, leading by addition of oxygen to the alpha-peroxy radical species

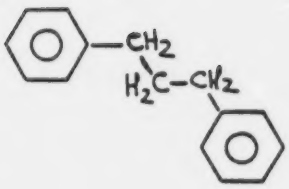
Ar.(CH.O-O.)(CH2)n-1.Ar

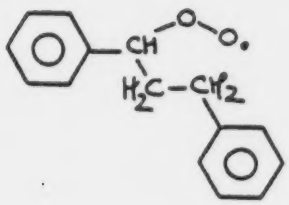
which may abstract hydrogen from further along the chain, or from an adjacent chain, to form the hydroperoxy species with a radical center further along the chain or at an adjacent chain. Reaction with a further oxygen molecule would give a hydroperoxy - peroxy species, e.g.

Ar.(CH.O-OH).CH2.(CH.O-O.).(CH2)n-3.Ar

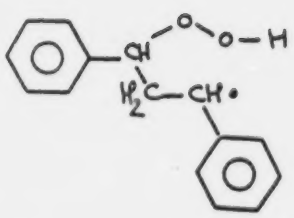
This may fragment into a ketonic species and a carboxylic acid species, accounting for the evidence of concurrent formation of both species at fairly early stages of moderate-temperature coal oxidation.

The suggested mechanism for this process is illustrated in the accompanying figure. It is based upon analogies with the high-temperature oxidative fragmentation of long-chain alkane species.

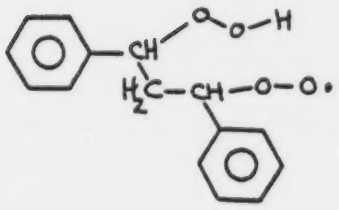




PEROXY RADICAL

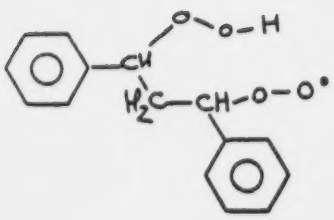


(HYDROPEROXIDE + RADICAL)



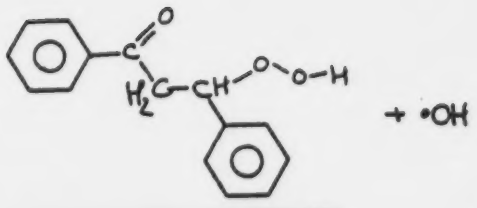
ALPHA HYDROPEROXIDE

GAMMA PEROXY



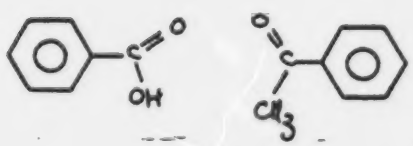
ALPHA HYDROPEROXIDE

GAMMA PEROXY



ALPHA-KETO GAMMA-HYDROPEROXIDE

ALPHA, GAMMA CLEAVAGE



ARDIC ACID ARYL METHYL KETONE

POSTULATED MECHANISM BASED ON

S. KORCEK ET AL.,

J. AM. CHEM. SOC. 103, 1742-1749 (1981)

Simultaneously with fragmentation, conversion of simple monohydroperoxides into aryl alkyl ketones and of diaryl ketones will occur.
Very recent work on the oxidation of alkylbenzene derivatives (see M. Pasternak and A. Morduchowitz, Tetrahedron Letters, Vol. 24, No. 40, 4275-4278 (1983)) confirms that the primary reaction point in such species is always a benzylic position.

As oxidation proceeds, the proportion of carboxylic acid species relative to the aryl alkyl ketones will increase, and at fairly advanced stages, many of the aromatic carboxylic acid groups should come to occupy adjacent (ortho) positions on the remaining aromatic skeletons.

If oxidation is performed at temperatures high enough for spontaneous dehydration of such ortho-related carboxylic acid groups, anhydrides of the type of phthalic anhydride should form readily.

The frequencies of maximal absorption of introduced carbonyl oxygen in the oxidized coals are distributed as unresolved envelopes between 1600 and 1800 cm.-1, but individual peaks are revealed by the device of quantitative methylation (as developed from previous work at St. Francis Xavier University). The approximate peak maxima in such methylated oxidized coals are found at the following positions for the various groups:

GROUP	FREQUENCY (cm.-1)
Vicinal Methoxycarbonyl	1730-1735
Isolated Methoxycarbonyl	1715-1720
Aryl alkyl ketone where aryl group lacks methoxy functions	1695-1705
Aryl alkyl ketone where aryl group carries methoxy functions	1670-1685
Diaryl ketone or anthrone type	1635-1650

The patterns of behavior shown after the methylation treatments by the various samples of naturally weathered and artificially oxidized coals are consistent with the generation and the progressive transformation of all of the types of oxygen functionality suggested above.

In addition, there is no evidence for the generation of other non-carbonyl oxygen groups during the course of oxidation.

Our observations from the spectra of the derivatized coals show in fact that without extreme precautionary measures, there may be no such thing as an "un-oxidized" experimental coal sample, since there is significant discrete absorption at 1700 cm.-1 or thereabouts in the methylated conversion products from so-called "fresh" coal samples.

NATURAL WEATHERING AND ACCELERATED ARTIFICIAL OXIDATION OF THE COAL SAMPLES

This section of the report is devoted to a comparative analysis and comparison of the oxidation patterns exhibited by the suite of coals and of a range of other reference coal samples, and also treats various methods of assessment of the extent of oxidation.

(a) NATURAL OXIDATION

The first examples illustrate the variation of the carbonyl (largely carboxyl) features in samples of naturally oxidized Ewin Pass bituminous coal at varying distances into the seam from the surface (20 metres and 22 metres). Figures 45 and 46 illustrate that for the demineralized (i.e., acid-treated) samples, the intensity ratios of the 1700 to 1600 cm.-1 features readily differentiate the extent of oxidation in the two species (compare Figure 47).

The PAIFT spectra of coal samples also differentiate readily between freshly obtained samples (CRL 82-1) and samples stored for approximately 2 years at common laboratory temperatures (CRL 82-11); this is shown in Figures 48 and 49.

(b) ARTIFICIAL OXIDATIONS

In the course of our research and development work for CANMET, we have developed the process of derivatization via phase-transfer methylation to enhance the features associated with the introduction of various types of additional carbonyl-type oxygens; the process might be termed "chemical deconvolution".

The enhanced resolvability is illustrated in Figures 50 and 51, representing the PAIFT of a sample of the CRL 82-1 coal oxidized for 2 weeks at 110 degrees.

Figure 52 reproduces the assigned functionalities and their progressive development in a series of methylated oxidized samples of Cape Breton coal examined in an earlier study.

However, for rapid indications of the extent of oxidation, a simpler procedure may be used.

As an example of the application of this generalized procedure, we normalized the PAIFT spectra of a series of samples of Devco metallurgical coal oxidized in a flow system at 100 degrees for periods up to 120 hours (see Figures 53 and 54).

The principal changes in the 2000-1550 cm.-1 region of the spectra (normalized to constant intensity of the 1600 cm.-1 feature) are that the high-frequency asymmetry of the band increases. Although no discrete carbonyl peaks appear at this level of

oxidation (the oxygen content changes from 10.2% for the initial state to 11.9 % for the most oxidized sample), increasing asymmetry is evident after as little as 14 hours.

Our review of oxidation (pp.59-61) indicated to us that most artificial oxidations are carried out without any specific provisions to match (even approximately) the weathering phenomena of outcrop coal or stored coals.

We reasoned that the thermal oxidation of coal might be accelerated if the coal sample were irradiated during the course of oxidation experiments (corresponding to exposure to sunlight).

A series of experiments was therefore performed involving oxidation of series of coals and of separated maceral constituents, where the experimental conditions involved irradiating the finely powdered coal situated approximately 10 cm under a 300 W Photoflood lamp, providing a surface temperature of approximately 90 degrees. This experimental configuration is similar to that used by Montgomery and co-workers in some aspects of their studies of oxidation of coking coals (B. S. Ignasiak, B. N. Nandi, and D. S. Montgomery, Fuel, 49, 214 (1970); B. S. Ignasiak, D. M. Clugston, and D. S. Montgomery, Fuel, 51, 76 (1972)).

The initial experiments involved placing a maceral sample directly into the sample cup of the photoacoustic cell, and repeated sampling of the PAIFT spectrum as oxidation proceeded. The samples examined in this manner were separated macerals from coals in the Pennsylvania State University coal bank, including two inertinite fractions and a vitrinite concentrate from PSOC # 106-2 (provided by Dr. G. R. Dyrkacz, Argonne National Laboratory, Illinois), and a sporinite sample from Barnsley, U. K. (provided by Dr. J. Allan, Esso Resources, Calgary). The developing carbonyl features in these samples with increasing irradiation time are illustrated in Figures 55-58, and Figure 59 generalizes the information. In Figure 59, the plotted ordinate scale is ten times the asymmetry ratio minus one (i.e. 2 corresponds to an asymmetry ratio of 1.2); the abscissa is in hours of irradiation. In all of the PSOC-106-2 samples (which are very finely divided, (less than 1 micrometer particle size)) it is evident from the high-frequency asymmetry of the 1600 cm.-1 features that the initial samples (before any irradiation) are significantly oxidized.

There is, in fact, a general correspondence between the asymmetry of the 1600 cm.-1 feature and the oxygen content of coals, ranging through high-volatile bituminous through to sub-bituminous: this point is illustrated by Figures 60 and 61. Figure 60 displays the normalized 1600 cm.-1 band features (i.e. scaled to constant intensity) versus analyzed oxygen content for a series of U. K. vitrinite concentrates containing varying proportions of oxygen. There is a good linear relationship (displayed as Figure 61) between the total peak area between 1600 and 1800 cm.-1 and the observed oxygen content.

In view of the results from irradiative oxidations of the selected macerals, we explored analogous oxidations of the various coals supplied by the Coal Research Laboratory. Powdered samples for irradiation were spread as thin layers on watch glasses and portions were removed at specified intervals and their PAIFT spectra were recorded. The portion size was sufficient (ca. 200 mg) for later derivatization by methylation or acetylation procedures.

The progressive changes were monitored for the following coals: CRL 82-1, 82-3, 82-7, 82-8, 82-9, 82-10.

Figures 62 and 63 reproduce the spectra of CRL 82-1 (Harmer Seam bituminous), and Figure 64 displays the development of intensity in the carbonyl region. Difference spectra for the 1900-1550 cm.-1 region, obtained by an optimized subtraction subroutine, are given in Figures 65 through 68 for various irradiation times, and the areas of the carbonyl absorptions are plotted against irradiation time in Figure 69. For this coal sample and set of conditions, the starting coal was virtually free of added carbonyl functionality. The frequency of maximum difference changes from around 1650 cm.-1 for the initial stages of irradiation (20 hr, Figure 65)(assignaed to ketone carbonyls) to 1705 cm.-1 for later stage (118 and 166 hr, Figures 67, 68). Peaks around 1720 cm.-1 changing to shoulders on the 1705 cm.-1 band are assigned to carboxylic acid functions not hydrogen-bonded to other oxygen-containing groups, while the 1705 cm.-1 peak is assigned to hydrogen-bonded carboxylic groups.

The difference plot (Figure 69) indicates that there are two sequential sets of oxidation, which it is tempting to assign to the formation of (ketones + acids) (see scheme on p. 63) followed by ketone to acid conversion.

As noted above and reported upon previously, methylation of oxidized coals enhances the resolvability of carbonyl features. Figures 70 and 71 illustrate this point for the full spectra of methylated CRL 82-1 and the methylated irradiation product from 118 hr exposure of CRL 82-1. Figures 72 and 73 indicate a more extended overlay sequence for varying irradiation periods, and Figure 74 illustrates the development of the specific carbonyl features in the series of methylated irradiated samples. The series of difference spectra reproduced as Figures 75 through 80 confirm the proposed course of reaction suggested above from the difference spectra of the underivatized samples. Thus at the earliest stages of oxidation (20 hr irradiation), there are several distinct carbonyl peaks (Figure 75), while for more extended oxidation (118 hr, 166 hr) the oxygen functionality is dominated by a single type (aromatic methoxycarbonyl).

Coal CRL 82-3 (McIntyre Mines bituminous) shows a generally parallel behavior: thus Figure 81 illustrates the developing carbonyl absorption, and Figures 82-84 are selected corresponding difference spectra. Figure 85 shows the carbonyl development in the methylated irradiated coals, and Figures 86 and 87 the change in distribution of carbonyl type with time. The data of Figure 85 may be curve-fitted to a parabolic relationship, illustrated in Figure 88.

Coal CRL 82-7 (British Petroleum bituminous) behaves in a different manner to the above two coals.

Although the general features and trends are similar, as illustrated by Figure 89 (development of carbonyl features with time), the difference spectrum of the most extensively oxidized coal (166 hr, figure 90) indicates that the introduced carboxylic acid groups are probably not in a hydrogen-bonded environment. This could be rationalized since CRL 82-7 is the highest rank coal in the set in terms of C/O ratio, and it lacks sufficient initial oxygen content to hydrogen-bond to formed carboxylic acid groups. Although Figure 91 represents the post-methylated samples as for the above samples, the difference spectra for 32 hr oxidation indicate that methoxycarbonyl groups dominate the carbonyl content (i.e. carboxylic acids and ketones are not being co-generated). This may be explained if coal CRL 82-7 has a larger proportion of its aliphatic carbon in the form of methyl, rather than methylene groups.

The pattern of behavior for coal CRL 82-8 (Coleman Collieries bituminous) is generally similar to CRL 82-1 and 82-3 (see Figures 94-98) and no detailed comment is offered.

Coal CRL 82-9 (Judy Creek sub-bituminous, cleaned sample) was not examined in great detail; the major point is that the rate of oxidation of this coal was far slower than for any of the bituminous coals; also, difference spectra are difficult to quantify (see, for example, Figures 99 and 100) since there are changes in many of the peak intensities rather than changes being confined to carbonyl species.

Finally, coal CRL 82-10 (Cardinal River bituminous) was examined. Figure 101 illustrates the progressive changes in the total PAIFT spectra with irradiation time, and Figures 102-104 some corresponding difference spectra. The development of carbonyl features in the methylated irradiated coals is illustrated in Figure 105 and further in Figure 106, and the changes in relative carbonyl peak area with time in the methylated irradiated coals are plotted in Figure 107.

(c) HIGH-TEMPERATURE OXIDATIONS

Fuller and his colleagues (ref. 11, see p. 61, this report) and Griffiths and his colleagues (ref. 10, see p. 61, this report) have recently examined oxidations of bituminous coals for brief periods at temperatures as high as 300 degrees. Fuller's group suggests that aryl carbonates are formed, while Griffiths suggests that aromatic acid anhydrides are generated. Our results from a brief survey of these reactions with some of the CRL series coals indicates very strongly that Fuller's proposal is incorrect. Thus, Figure 108 shows the carbonyl region of the PAIFT spectra for three typical Canadian bituminous coals oxidized at 300 degrees, and Figures 109 and 110 illustrate chemical changes and derivatization effected on one of the coals. Alkaline hydrolysis followed by methylation yields a product giving a carbonyl absorption indicative of vicinal methoxycarbonyl groups.

The materials from such oxidations have lost virtually all their aliphatic C-H functionality and might be interesting candidate materials for application of other physical methods of structure elucidation.

(d) ROOM-TEMPERATURE WEATHERING OF COAL: THE PROPOSALS OF LIOTTA AND CO-WORKERS

Liotta and his colleagues (ref. 6, see p. 61, this report) have claimed that the ambient-temperature weathering of Illinois # 6 bituminous coals forms additional ether-type functions, and the path of oxidation does not follow that we have suggested. In rebuttal of this conclusion we display Figures 111 and 112, which are PAIFT difference spectra of the actual experimental samples used by Liotta's group. It is evident that the patterns are consistent with those obtained in our experiments. Although there are differences in the 1200 cm.-1 region in our spectra, they reflect differences in the gypsum content of fresh and weathered sample material, which are exaggerated by the differential friability of coal and gypsum in the potassium halide pellets used for the FTIR work cited in Liotta's paper.

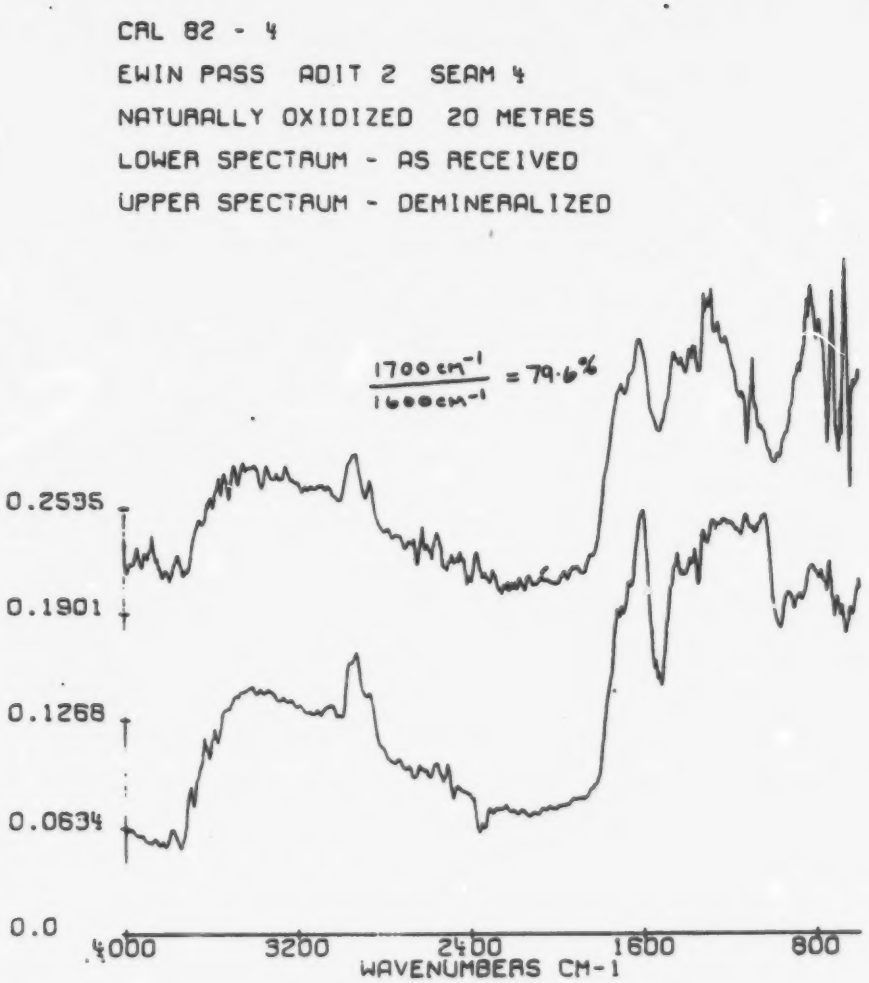

CAL 82 - 4
EWIN PASS ADIT 2 SEAM 4
NATURALLY OXIDIZED 20 METRES
LOWER SPECTRUM - AS RECEIVED
UPPER SPECTRUM - DEMINERALIZED
1700 cm-1 / 1600 cm-1 = 79.6%
0.2535
0.1901
0.1268
0.0634
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 45

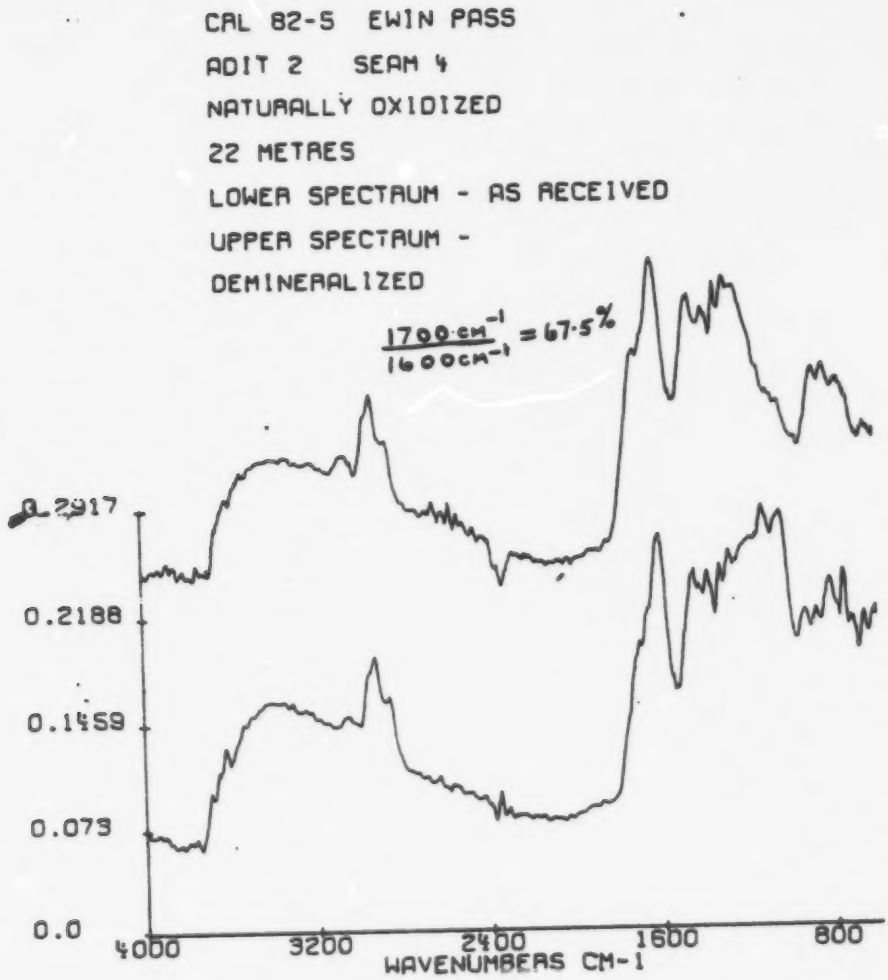

CAL 82-5 EWIN PASS
ADIT 2 SEAM 4
NATURALLY OXIDIZED
22 METRES
LOWER SPECTRUM - AS RECEIVED
UPPER SPECTRUM -
DEMINERALIZED
1700 cm⁻¹ / 1600 cm⁻¹ = 67.5%
0.2917
0.2188
0.1459
0.073
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 46

EWIN PASS NATURALLY OXIDIZED COAL
TOP 20 METRE DEPTH
BOTTOM 22 METRE DEPTH
1700/1600 CM.-1 INTENSITY RATIOS
ARE 0.80 AND 0.68 RESPECTIVELY

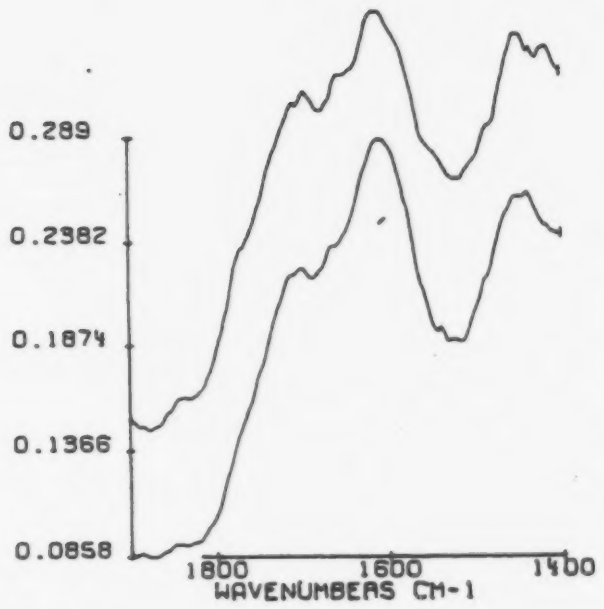


FIGURE 47

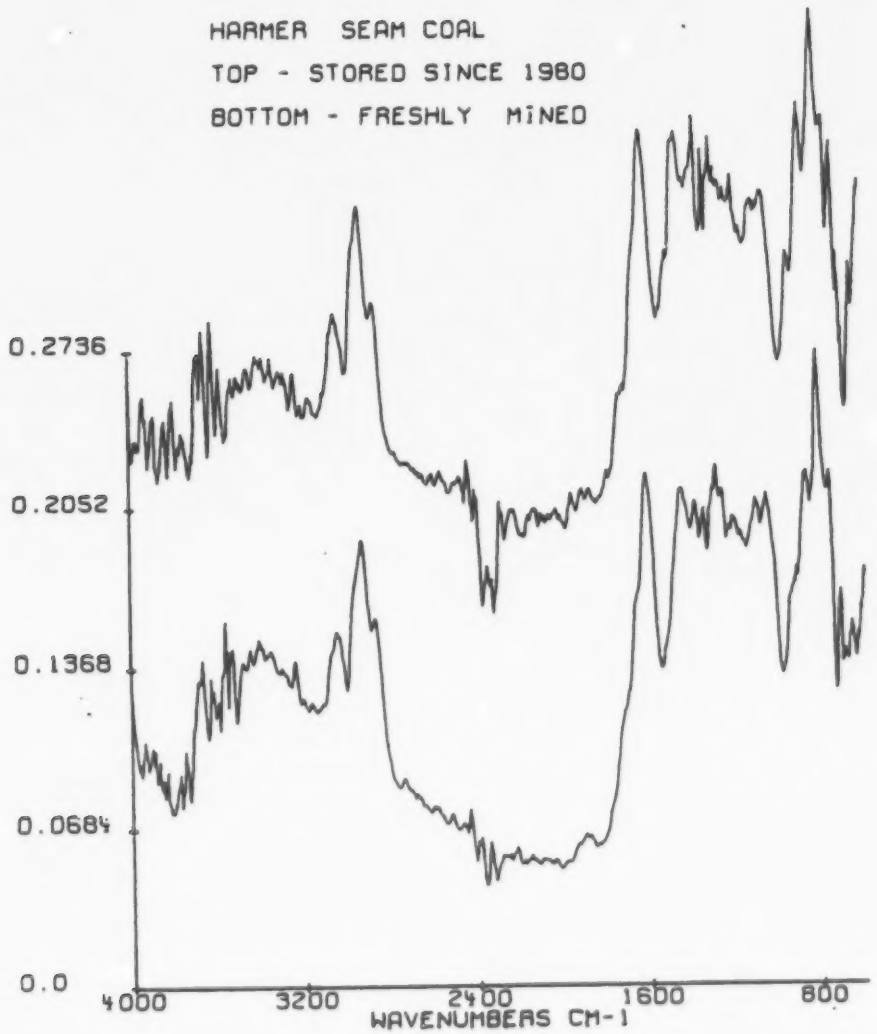

HARMER SEAM COAL
TOP - STORED SINCE 1980
BOTTOM - FRESHLY MINED
0.2736
0.2052
0.1368
0.0684
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 48

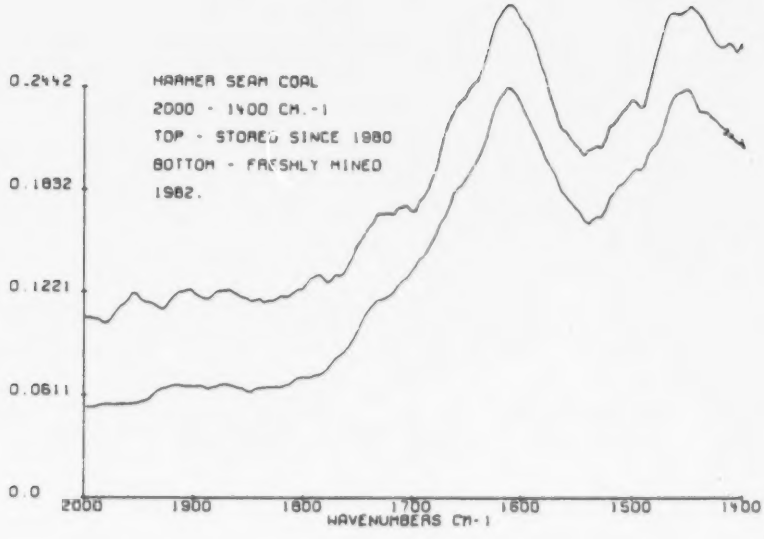

HAAMER SEAM COAL
2000 - 1400 CM.-1
TOP - STORED SINCE 1980
BOTTOM - FRESHLY MINED
1982.
0.2442
0.1832
0.1221
0.0611
0.0
2000
1900
1800
1700
1600
1500
1400
WAVENUMBERS CM-1

FIGURE 49

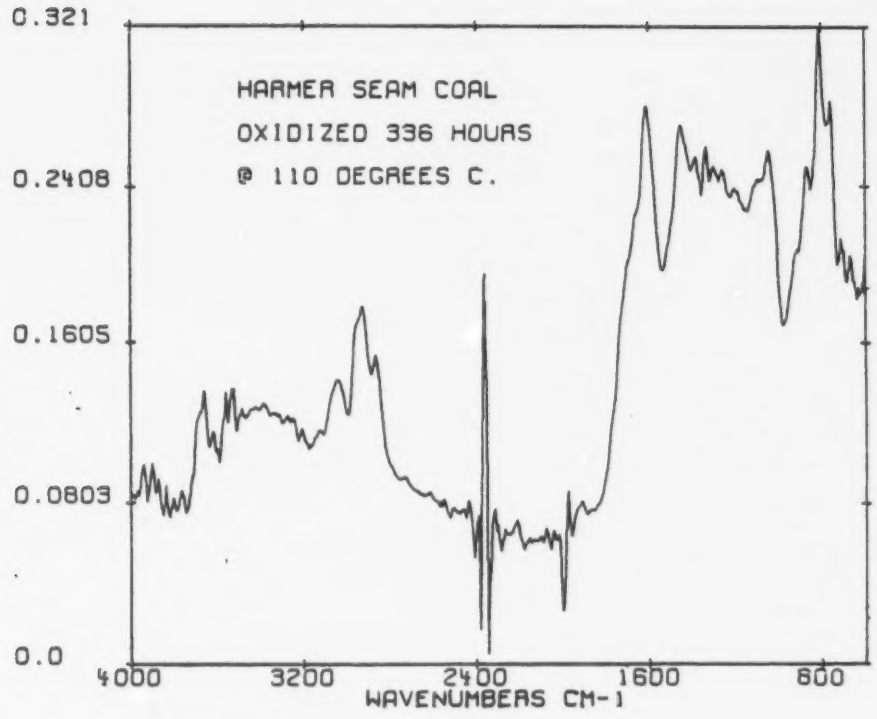

0.321
0.2408
0.1605
0.0803
0.0
HARMER SEAM COAL
OXIDIZED 336 HOURS
@ 110 DEGREES C.
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 50

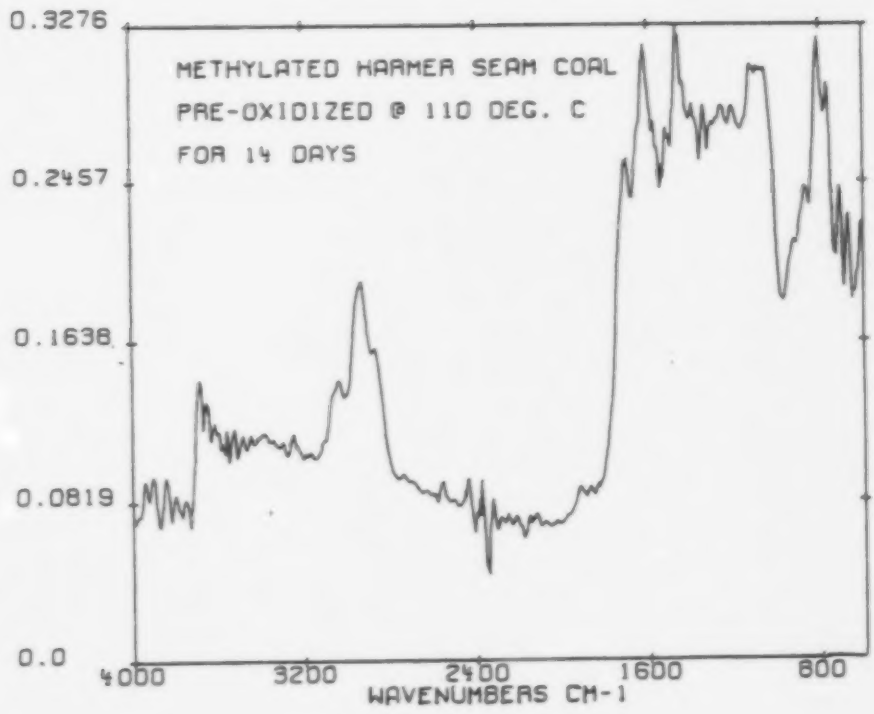

METHYLATED HARMER SEAM COAL
PRE-OXIDIZED @ 110 DEG. C
FOR 14 DAYS
0.3276
0.2457
0.1638
0.0819
0.0
4000
3200
2400
1600
800
WAVENUMBERS CM-1

FIGURE 51

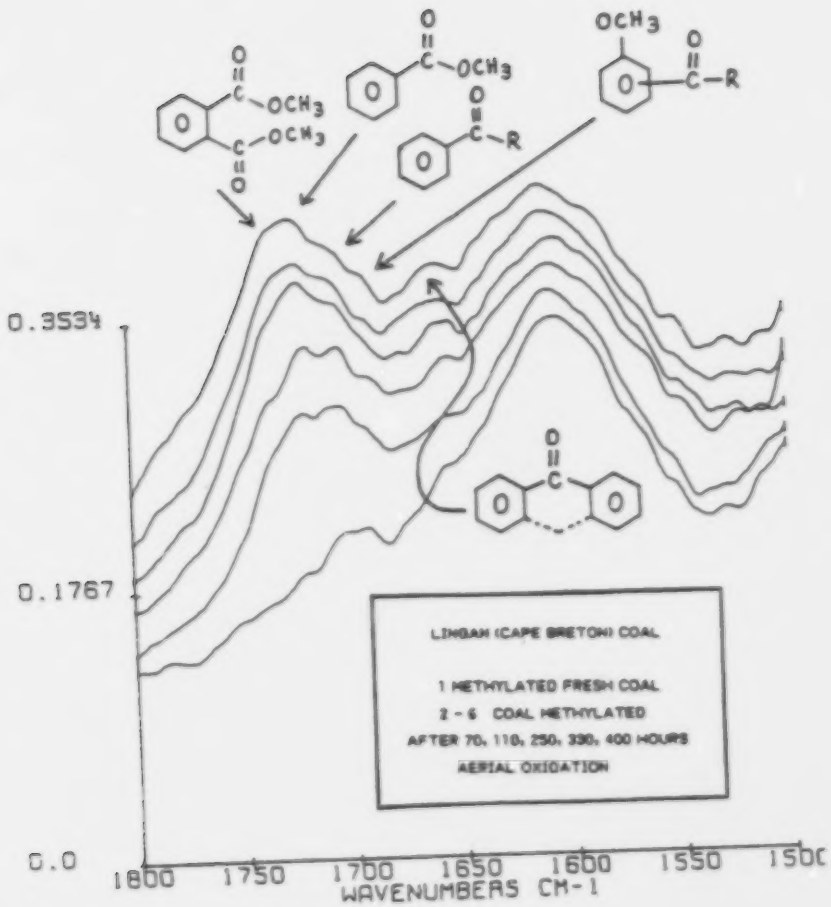

0.3534
0.1767
0.0
1800
1750
1700
1650
1600
1550
1500
WAVENUMBERS CM-1
LINGAN (CAPE BRETON) COAL
1 METHYLATED FRESH COAL
2 - 6 COAL METHYLATED
AFTER 70, 110, 250, 330, 400 HOURS
AERIAL OXIDATION

FIGURE 52

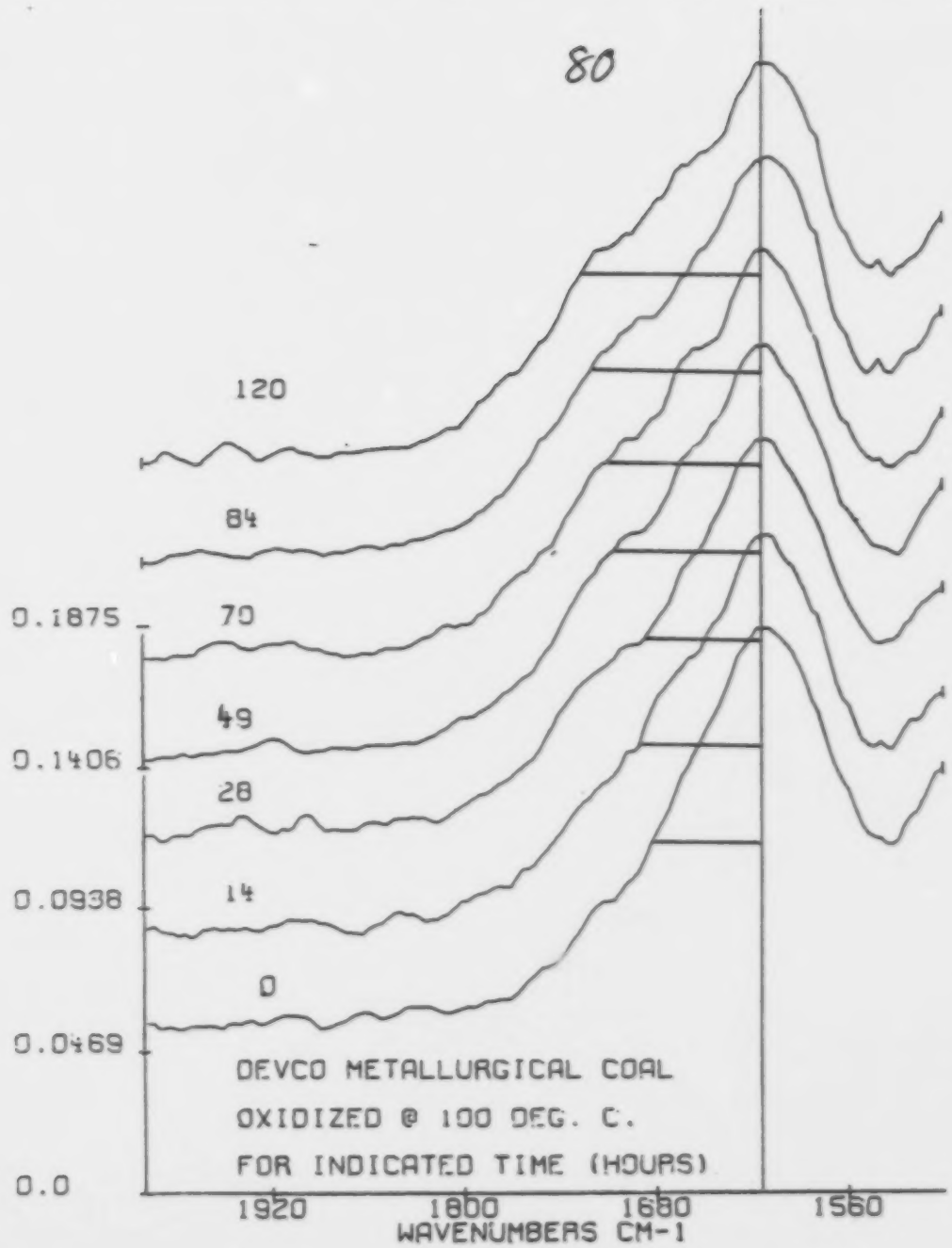
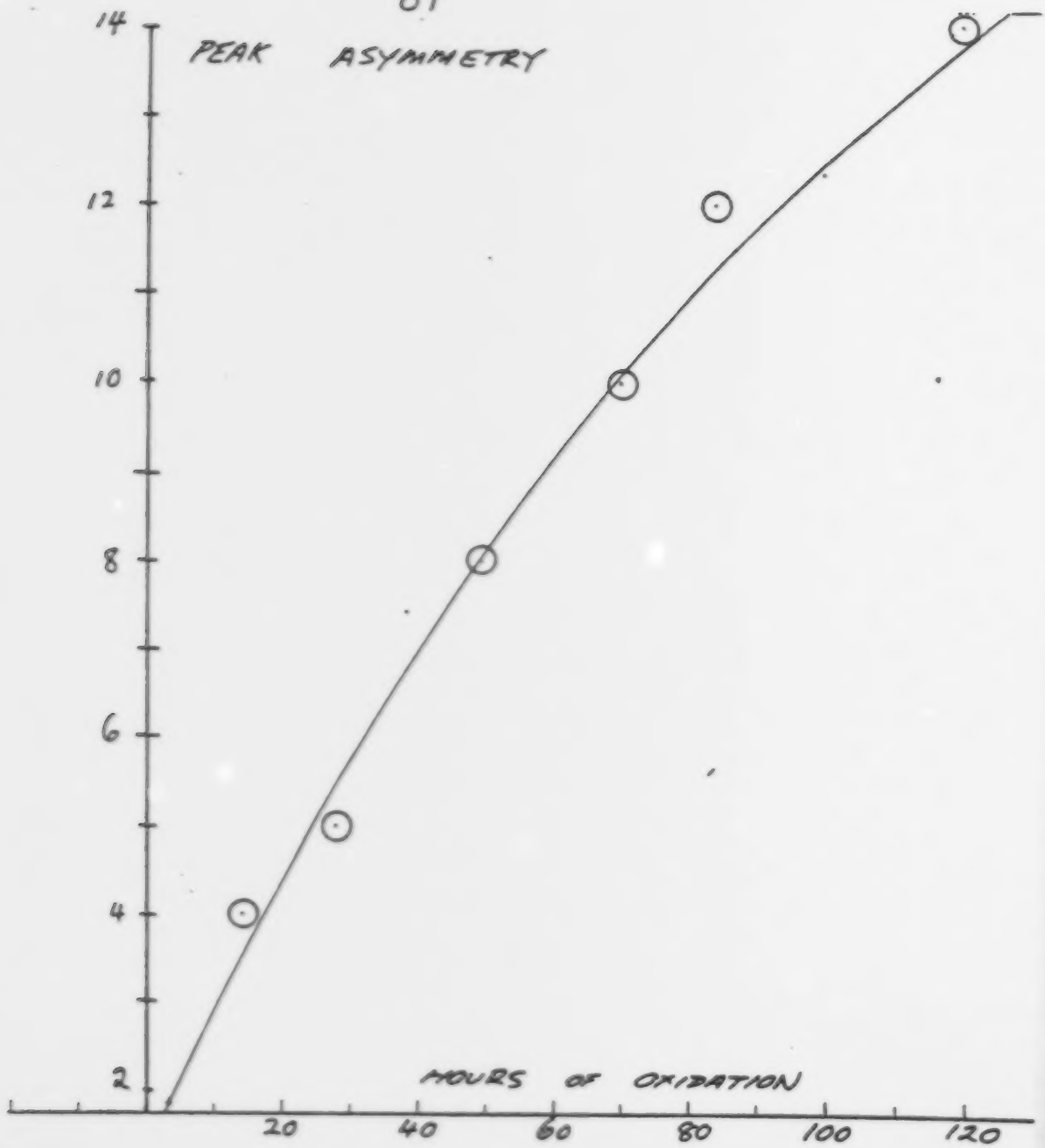

80
120
84
70
49
28
14
0
0.1875
0.1406
0.0938
0.0469
0.0
DEVCO METALLURGICAL COAL
OXIDIZED @ 100 DEG. C.
FOR INDICATED TIME (HOURS)
1920
1800
1680
1560
WAVENUMBERS CM-1

FIGURE 53



OXIDATION OF DEVCO METALLURGICAL COAL @ 100 DEGREES ; 1600 cm.$^{-1}$ ASYMMETRY vs. TIME

FIGURE 54

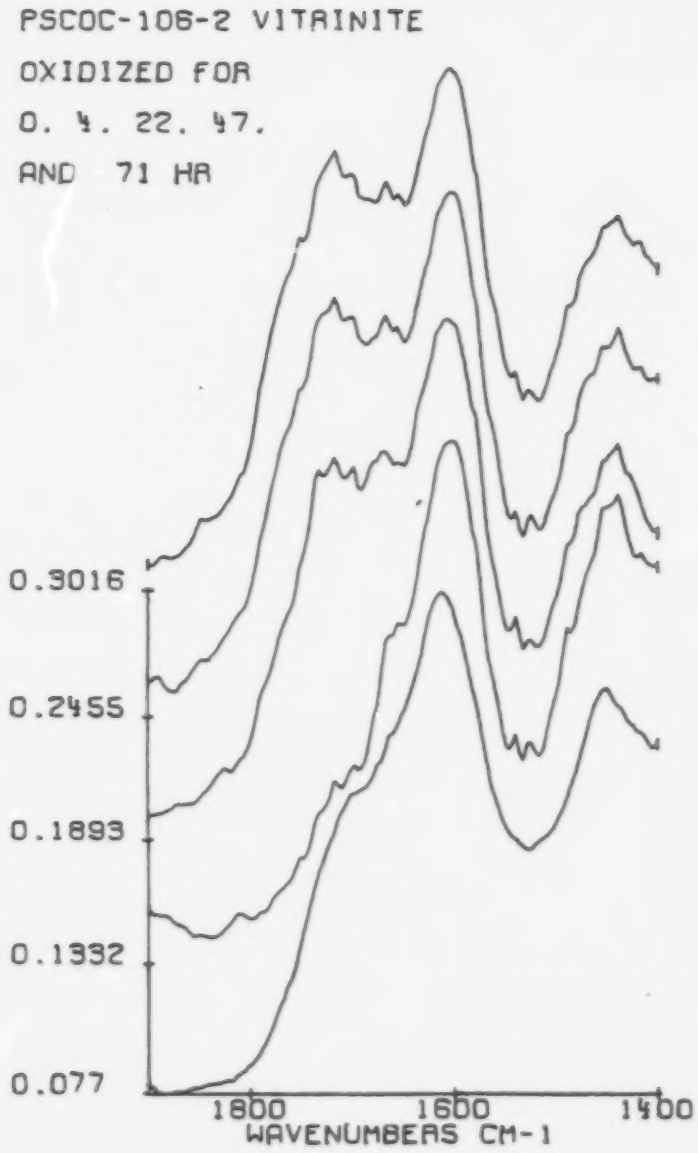

PSCOC-106-2 VITRINITE
OXIDIZED FOR
0. 4. 22. 47.
AND 71 HR
0.3016
0.2455
0.1893
0.1332
0.077
1800
1600
1400
WAVENUMBERS CM-1

FIGURE 55

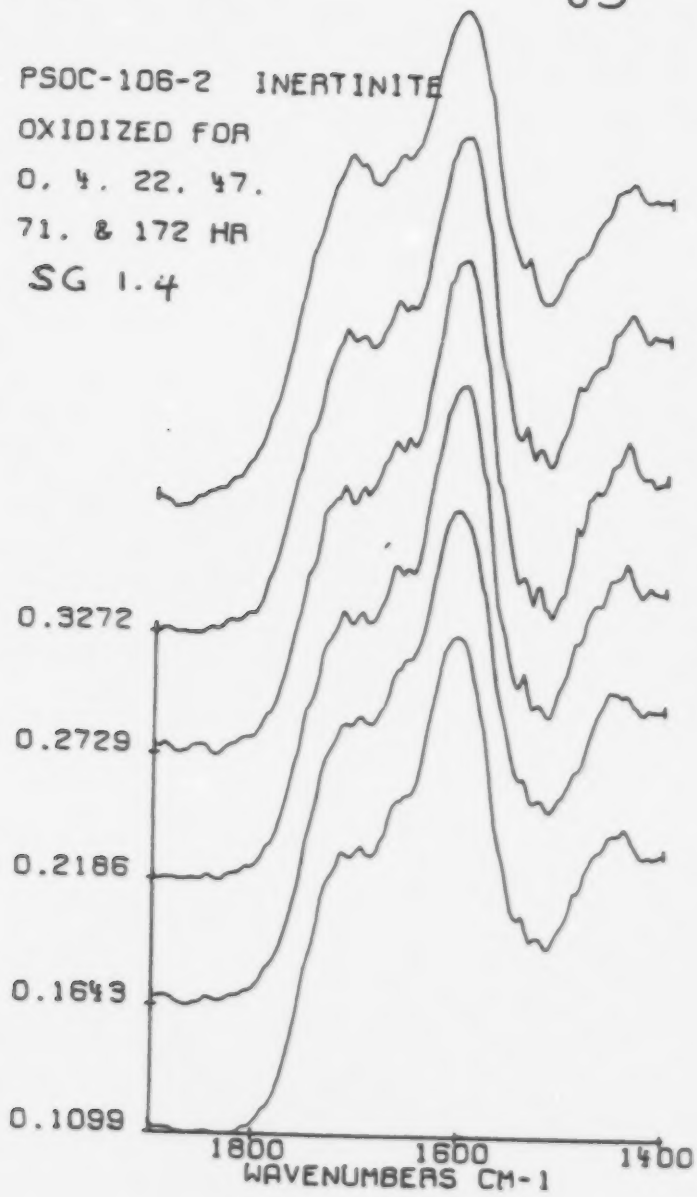

PSOC-106-2 INERTINITE
OXIDIZED FOR
0. 4. 22. 47.
71. & 172 HR
SG 1.4
0.3272
0.2729
0.2186
0.1643
0.1099
1800
1600
1400
WAVENUMBERS CM-1

FIGURE 56

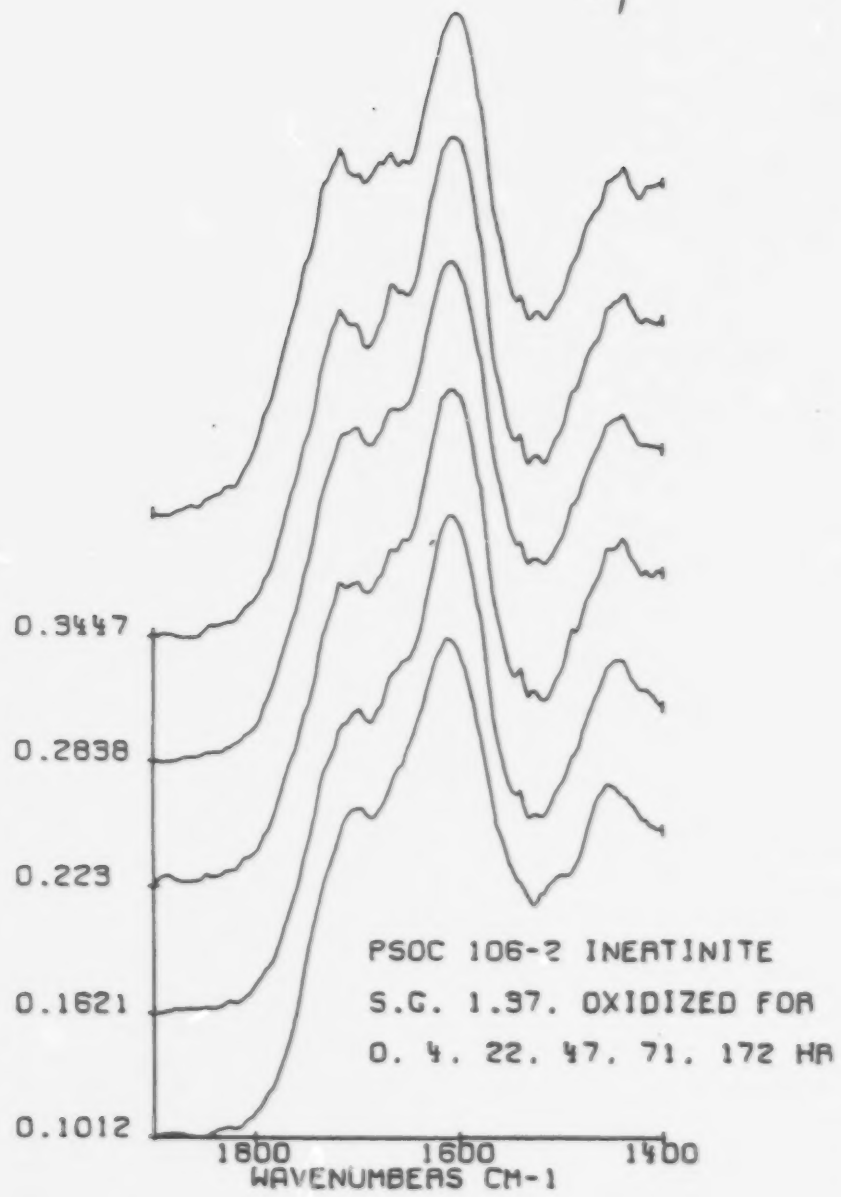

0.3447
0.2838
0.223
0.1621
0.1012
1800
1600
1400
WAVENUMBERS CM-1
PSOC 106-2 INERTINITE
S.G. 1.37. OXIDIZED FOR
0. 4. 22. 47. 71. 172 HR

FIGURE 57

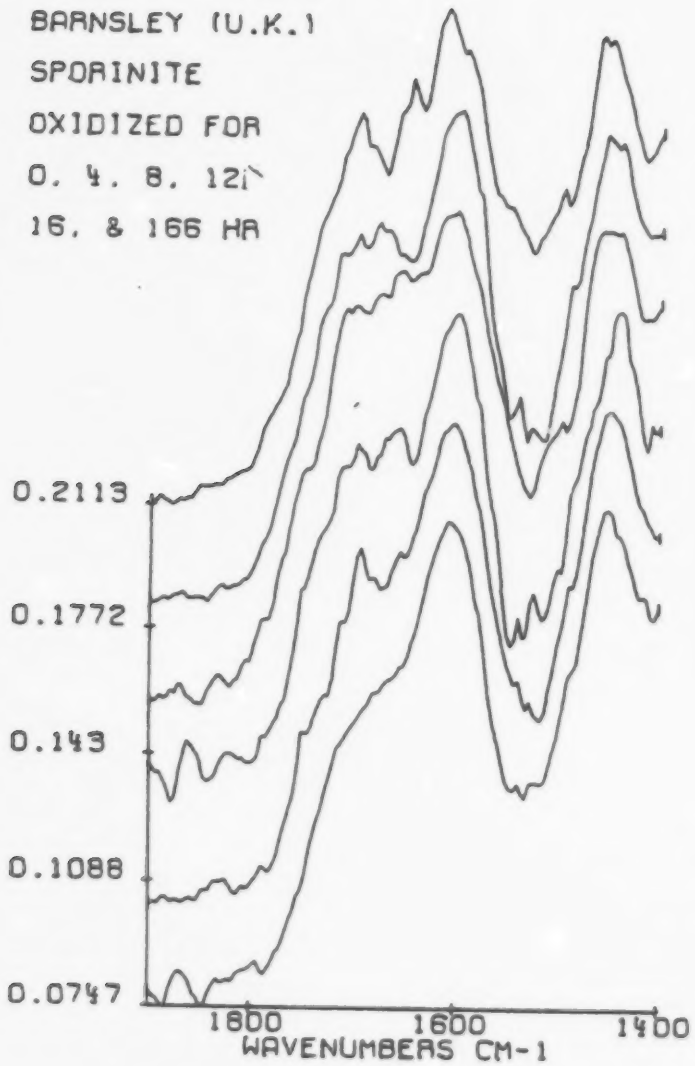

BARNSLEY (U.K.)
SPORINITE
OXIDIZED FOR
0. 4. 8. 12
16. & 166 HR
0.2113
0.1772
0.143
0.1088
0.0747
1800
1600
1400
WAVENUMBERS CM-1

FIGURE 58

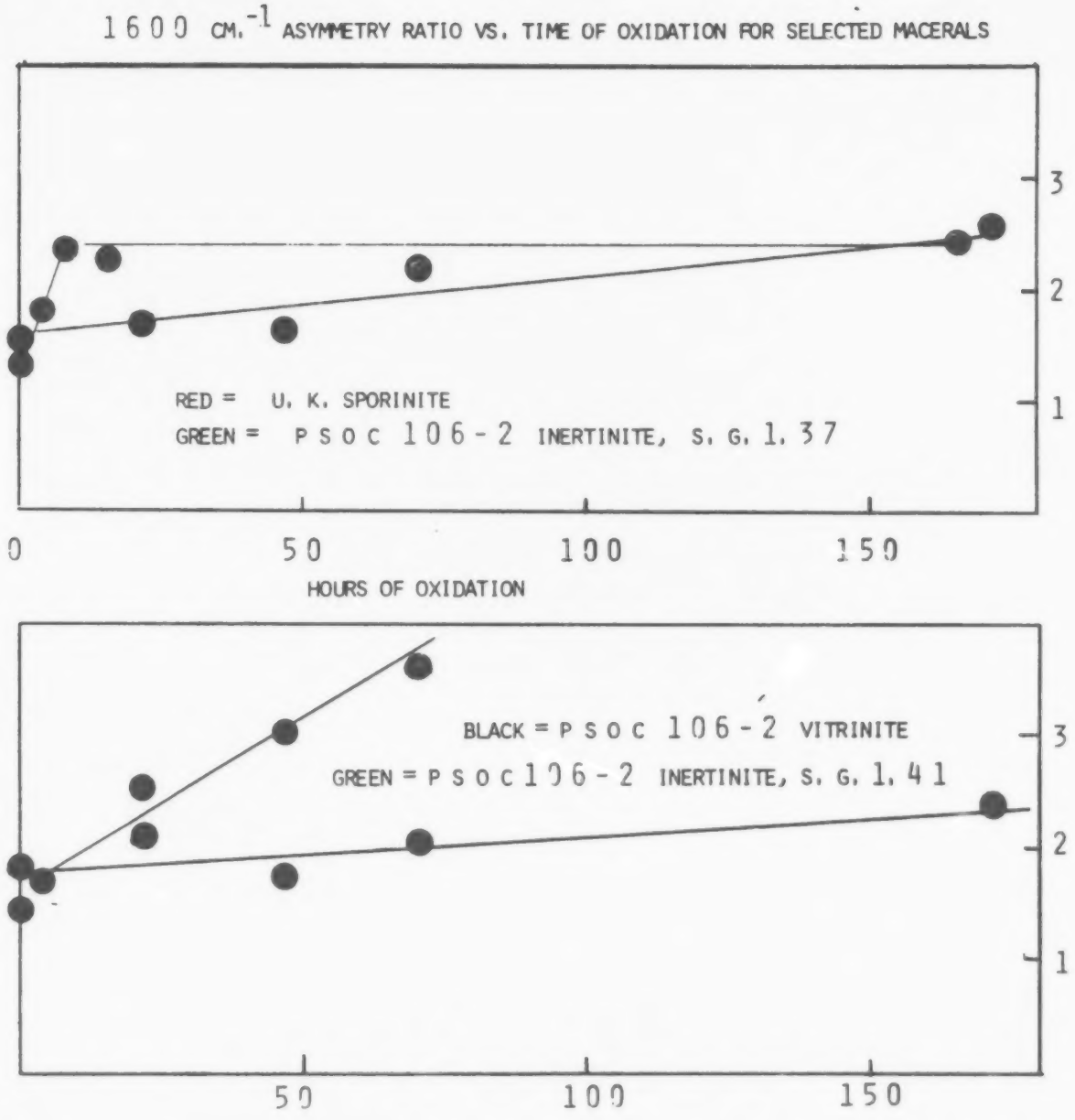
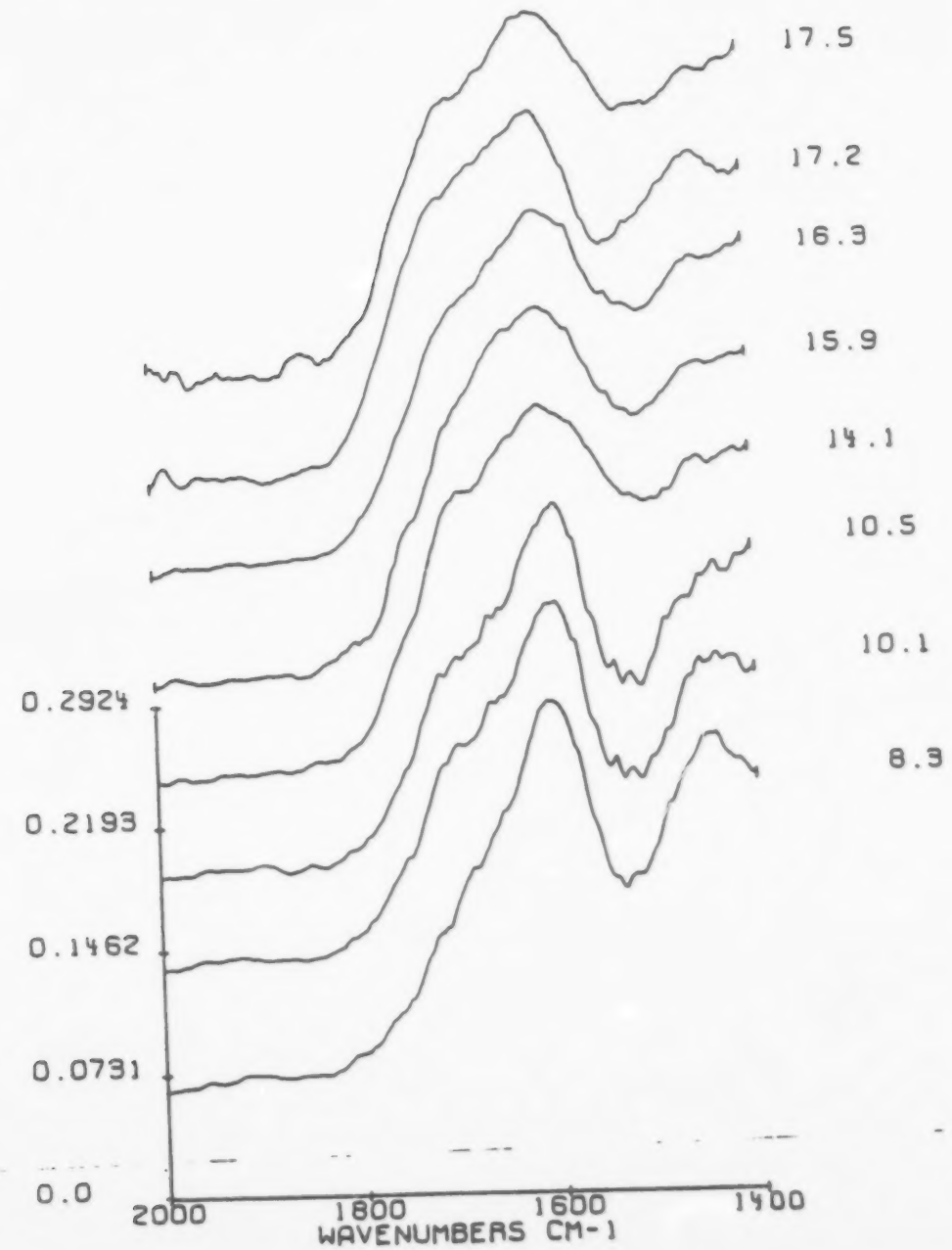

1600 CM.-1 ASYMMETRY RATIO VS. TIME OF OXIDATION FOR SELECTED MACERALS
RED = U. K. SPORINITE
GREEN = P S O C 106-2 INERTINITE, S. G. 1.37
0
50
100
150
HOURS OF OXIDATION
BLACK = P S O C 106-2 VITRINITE
GREEN = P S O C 106-2 INERTINITE, S. G. 1.41
1
2
3
50
100
150

FIGURE 59

U. K. VITRINITE CONCENTRATES

ASYMMETRY OF 1600 CM.-1 BAND
VS. OXYGEN CONTENT



U.K. VITRINITE CONCENTRATES

1600-1800 CM.-1 PEAK AREA VS. OXYGEN CONTENT

SAMPLE #	AREA (RELATIVE)	(CALCULATED)	OXYGEN (%)
V 8	1.000	1.006	8.3
V 7	1.006	1.050	10.1
V 6	1.040	1.060	10.5
V 5	1.235	OUTLIER	14.1
V 3	1.170	1.190	15.9
V 4	1.176	1.202	16.3
V 2	1.216	1.224	17.2
V 1	1.277	1.231	17.5

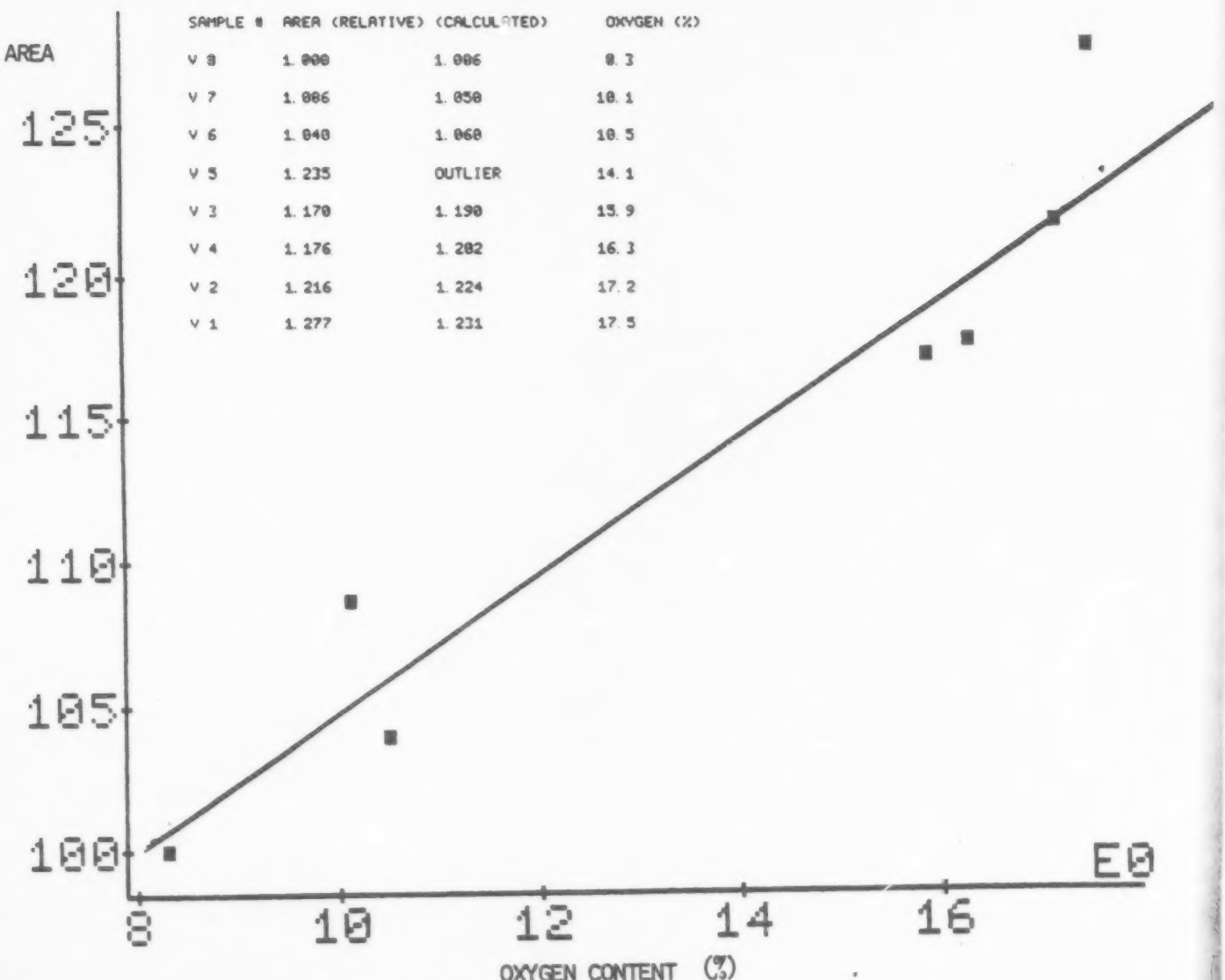


FIGURE 61

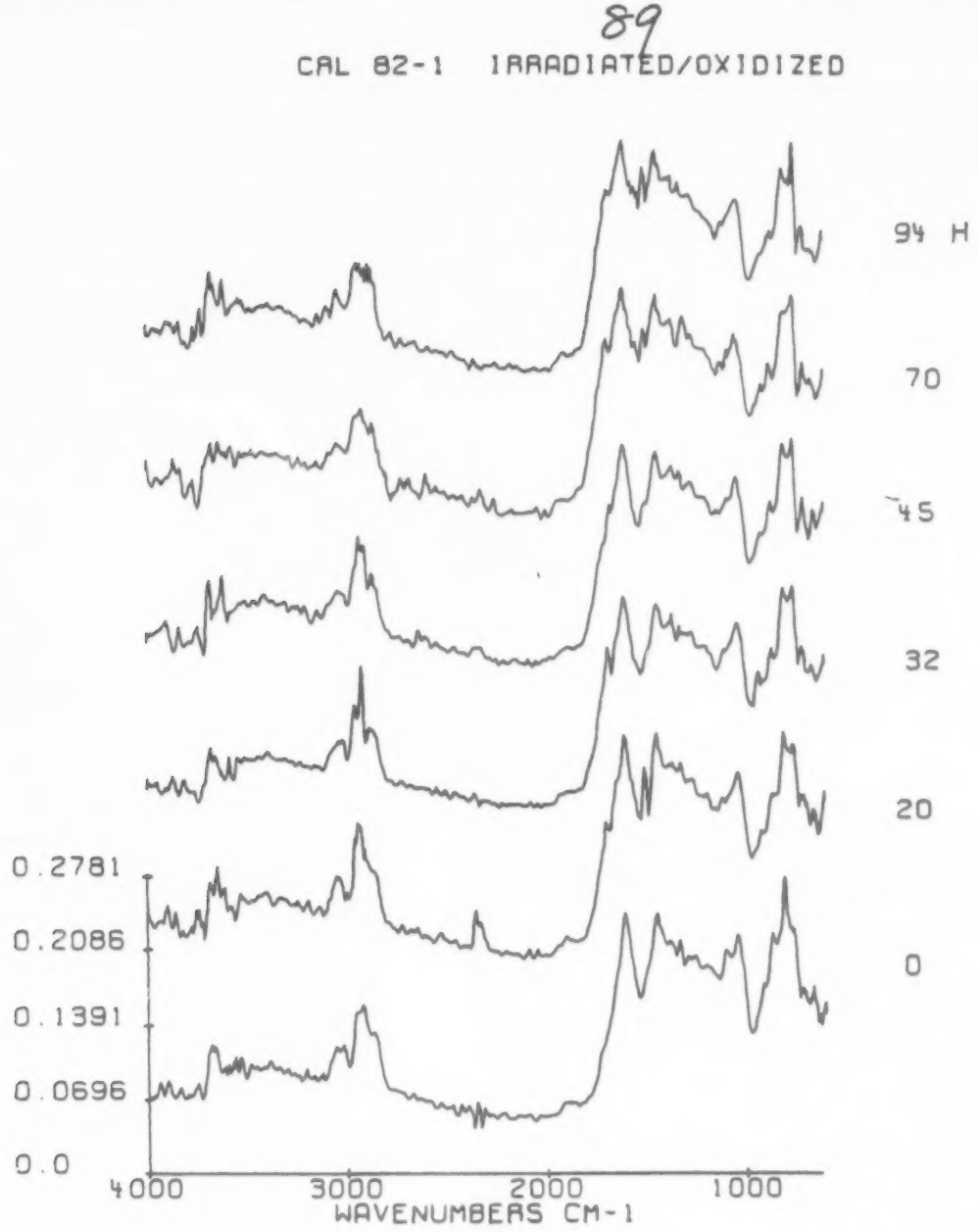

CAL 82-1 IRRADIATED/OXIDIZED
94 H
70
45
32
20
0
0.2781
0.2086
0.1391
0.0696
0.0
4000
3000
2000
1000
WAVENUMBERS CM-1

FIGURE 62

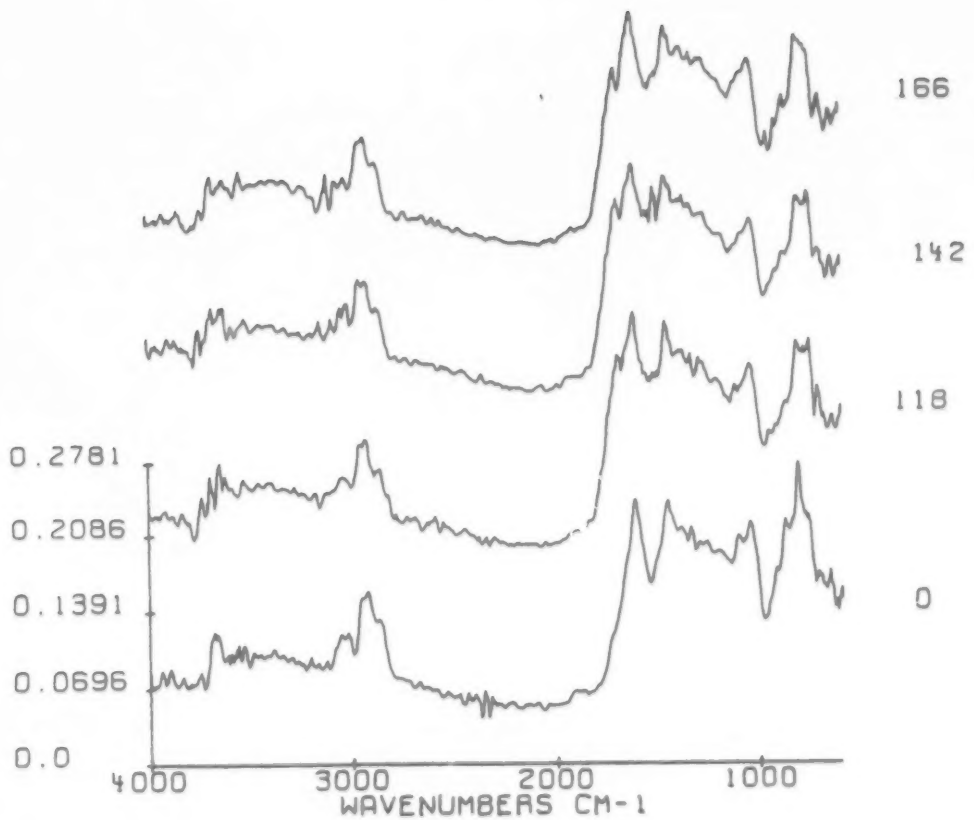

166
142
118
0
0.2781
0.2086
0.1391
0.0696
0.0
4000
3000
2000
1000
WAVENUMBERS CM-1

FIGURE 63

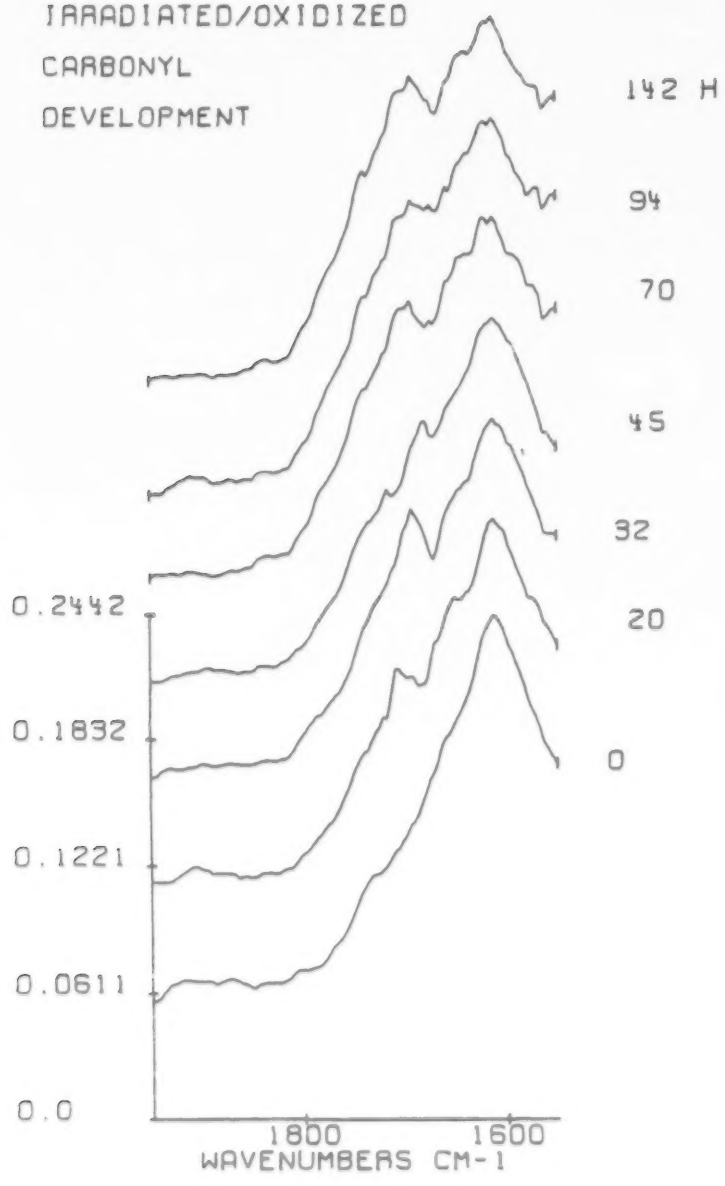

CAL 82-1
IRRADIATED/OXIDIZED
CARBONYL
DEVELOPMENT
142 H
94
70
45
32
20
0
0.2442
0.1832
0.1221
0.0611
0.0
1800
1600
WAVENUMBERS CM-1

FIGURE 64

DIFFERENCE SPECTRA

CRL 82-1

IRRADIATED 20 H VS FRESH

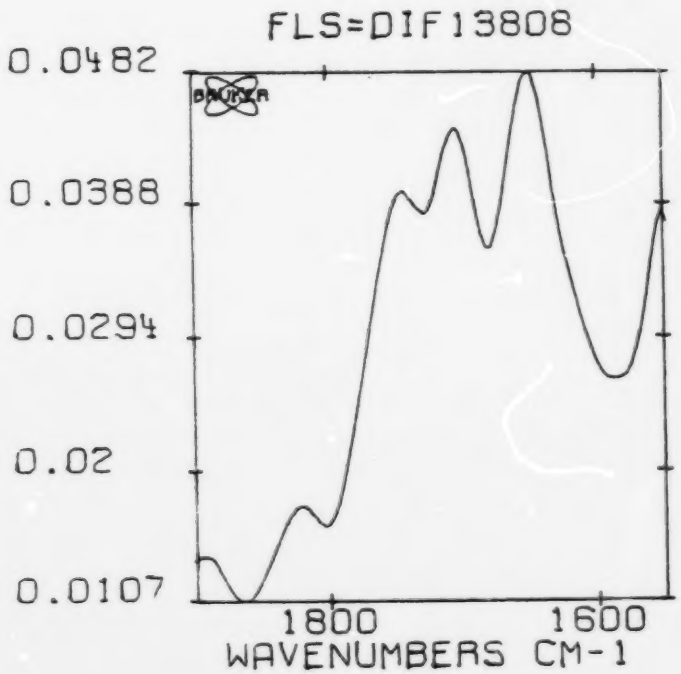


FIGURE 65

DIFFERENCE SPECTRA
CAL 82-1
IRRADIATED 32 H VS. FRESH

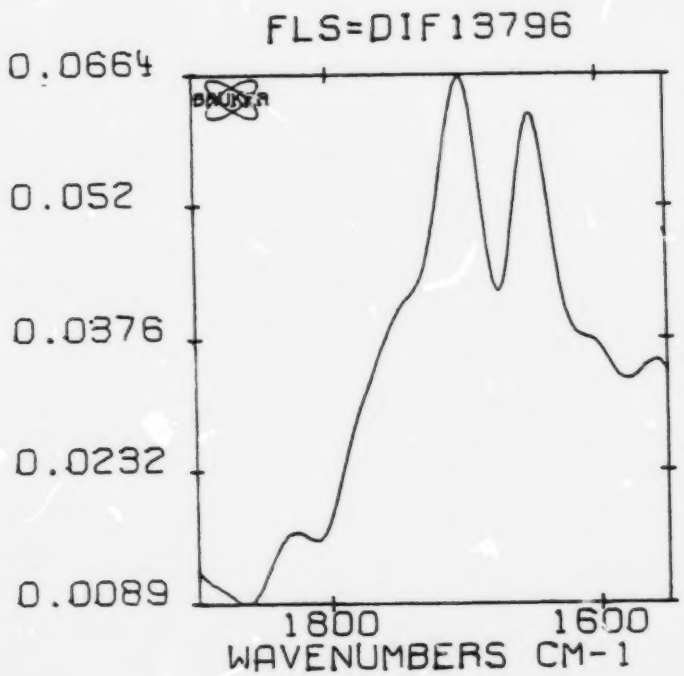


FIGURE 66

DIFFERENCE SPECTRA

CRL 82-1 IRRADIATED 118 H

VS. FRESH

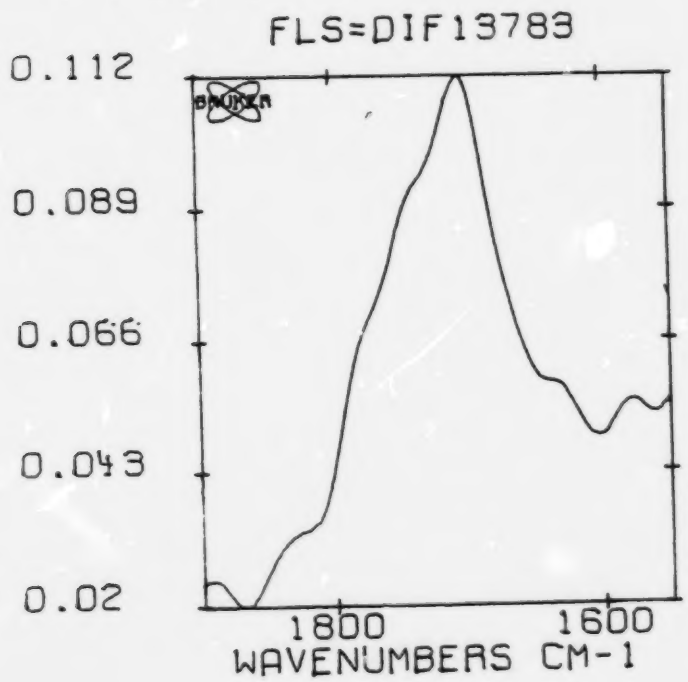


FIGURE 67

DIFFERENCE SPECTRUM
IRRADIATED CRL 82 - 1
166 HR - 0 HR

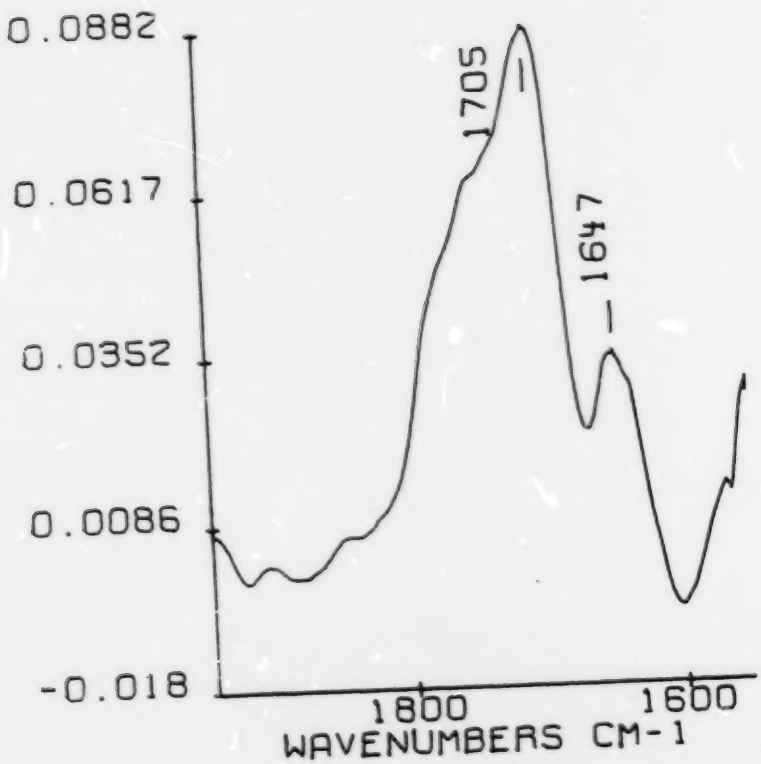
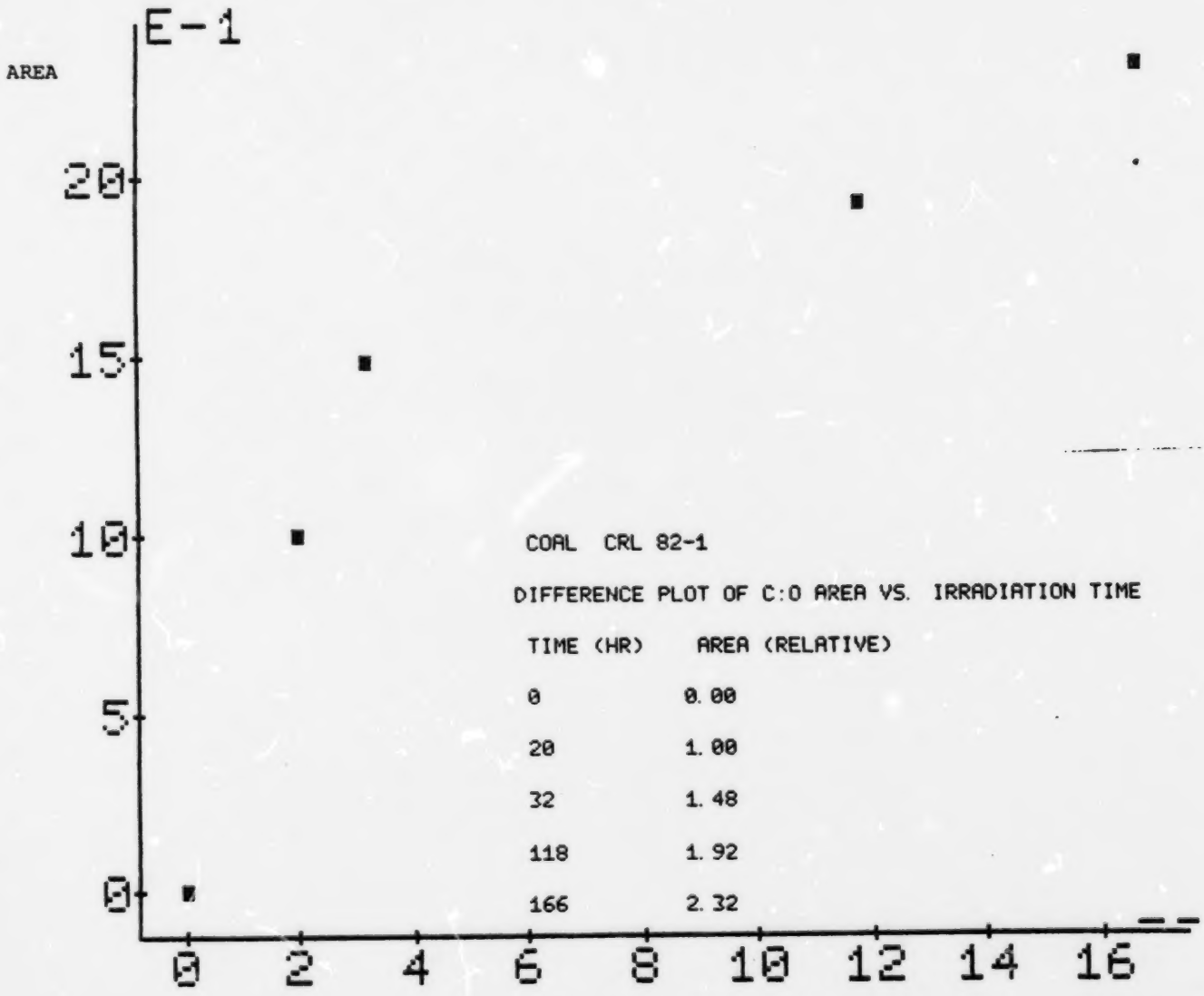


FIGURE 68



COAL CRL 82-1

DIFFERENCE PLOT OF C:O AREA VS. IRRADIATION TIME

TIME (HR)	AREA (RELATIVE)
0	0.00
20	1.00
32	1.48
118	1.92
166	2.32

FIGURE 69

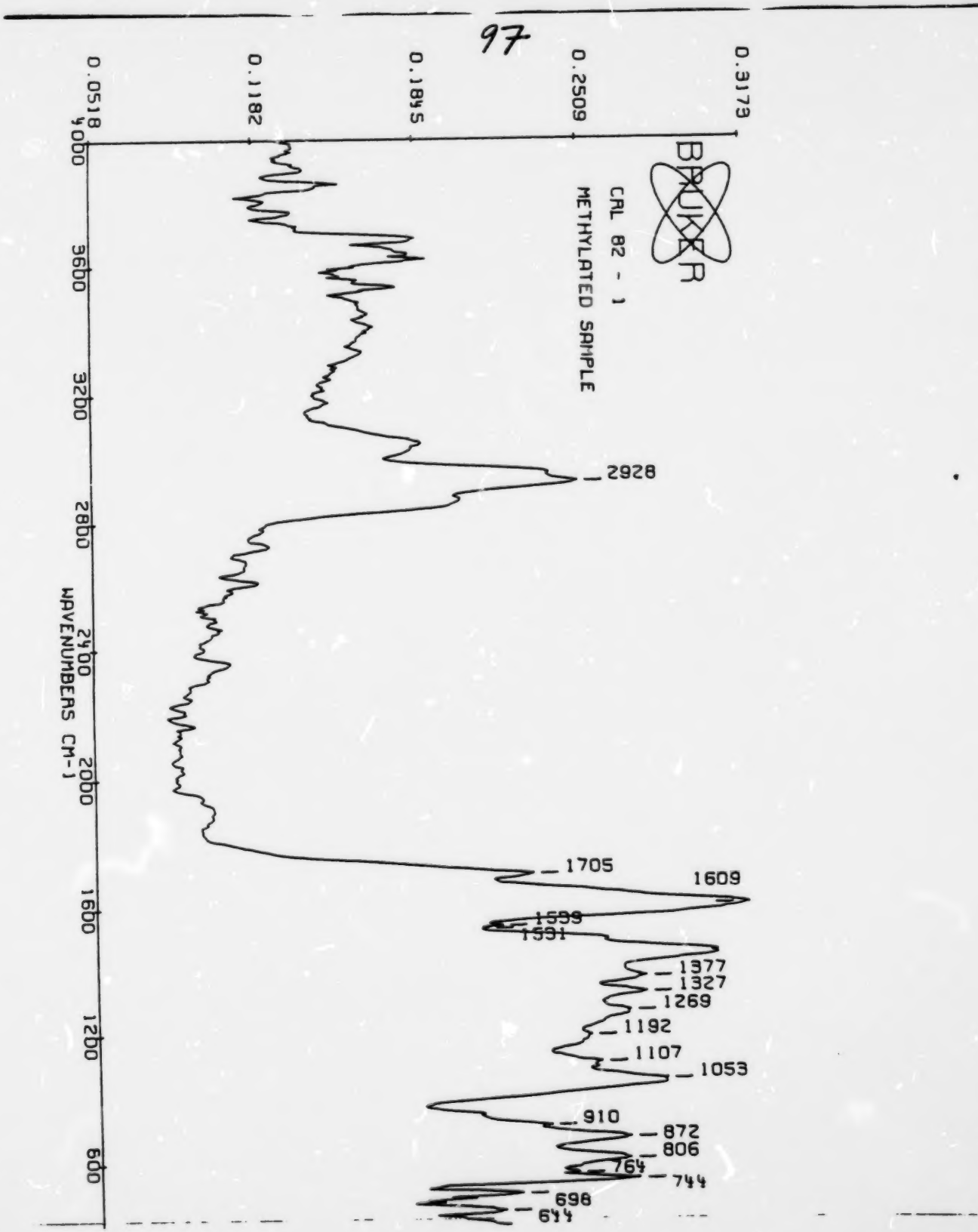

0.3173
0.2509
0.1845
0.1182
0.0518
BRUKER
CRL 82 - 1
METHYLATED SAMPLE
4000
3600
3200
2800
2400
2000
1600
1200
800
WAVENUMBERS CM-1
2928
1705
1609
1593
1591
1377
1327
1269
1192
1107
1053
910
872
806
764
744
698
644

FIGURE 70

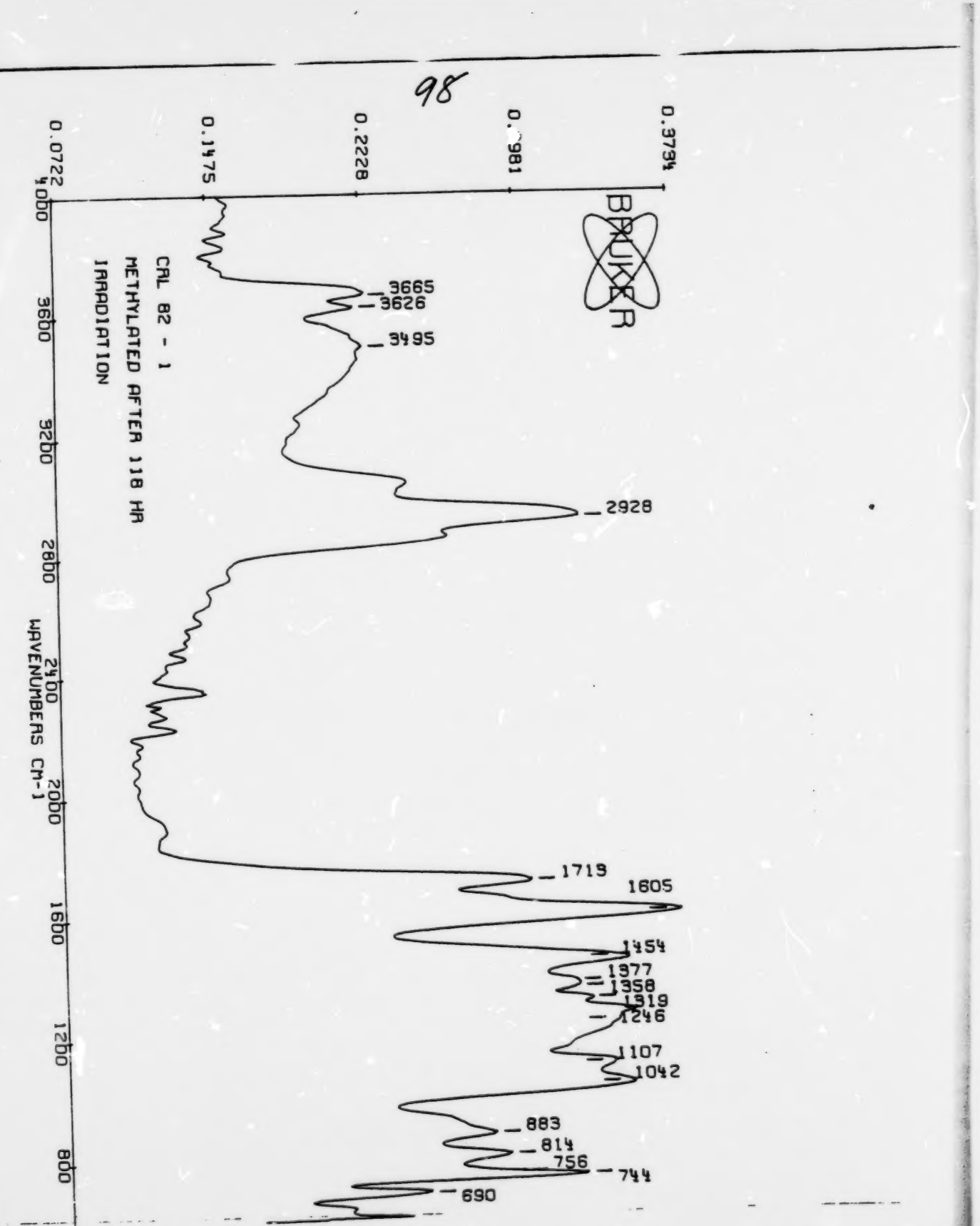
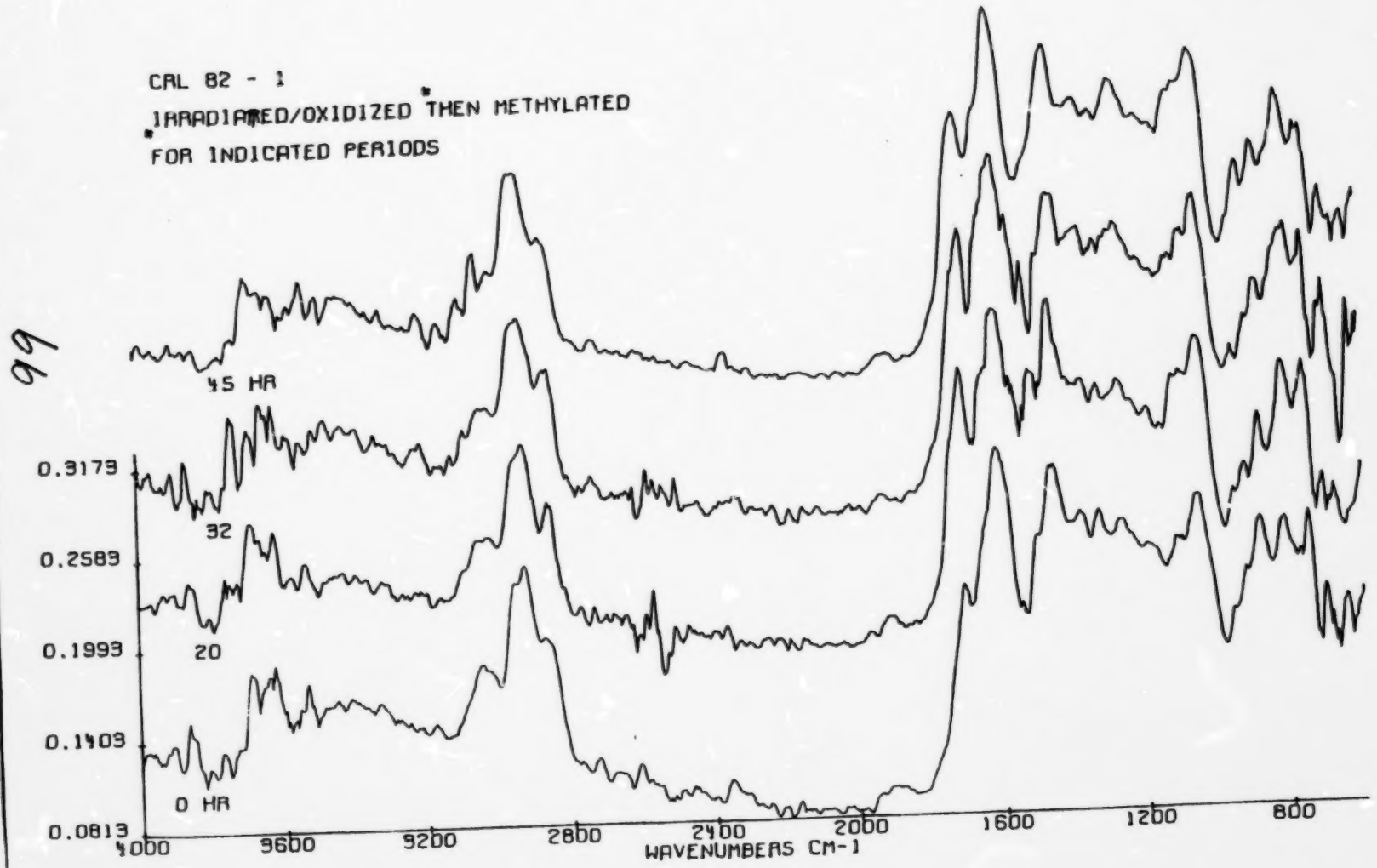

0.3734
0.2981
0.2228
0.1475
0.0722
4000
3600
3200
2800
2400
2000
1600
1200
800
WAVENUMBERS CM-1
CAL 82 - 1
METHYLATED AFTER 118 HR
IRRADIATION
BRUKER
3665
3626
3495
2928
1719
1605
1454
1377
1358
1319
1246
1107
1042
883
814
756
744
690

FIGURE 71


CAL 82 - 1
IRRADIATED/OXIDIZED THEN METHYLATED
FOR INDICATED PERIODS
45 HR
32
20
0 HR
0.3173
0.2583
0.1993
0.1403
0.0813
10000
9600
9200
2800
2400
2000
1600
1200
800
WAVENUMBERS CM-1

99

FIGURE 72

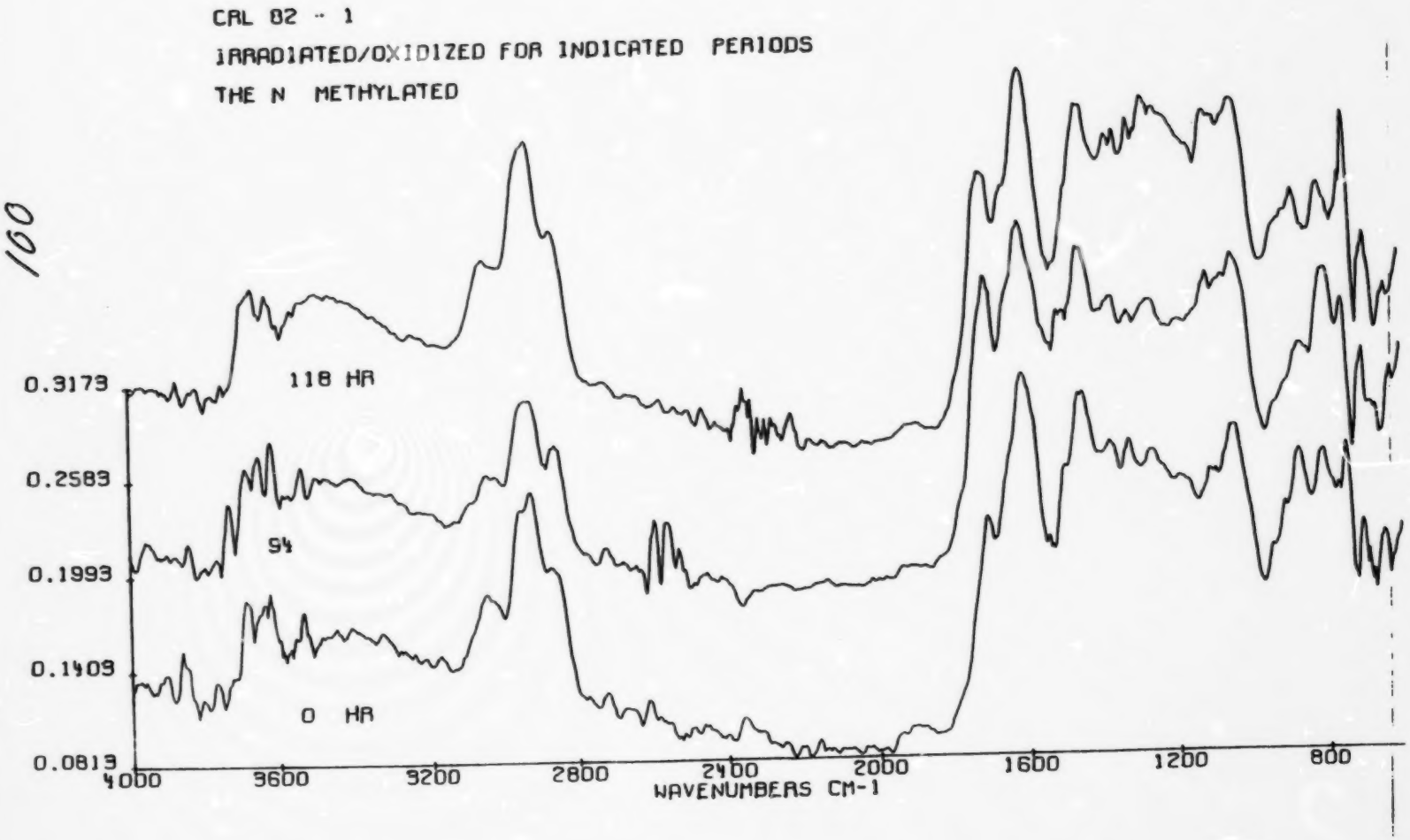

CRL 82 - 1
IRRADIATED/OXIDIZED FOR INDICATED PERIODS
THE N METHYLATED
160
0.3173
0.2583
0.1993
0.1403
0.0813
118 HR
94
0 HR
4000
3600
3200
2800
2400
2000
1600
1200
800
WAVENUMBERS CM-1

FIGURE 73

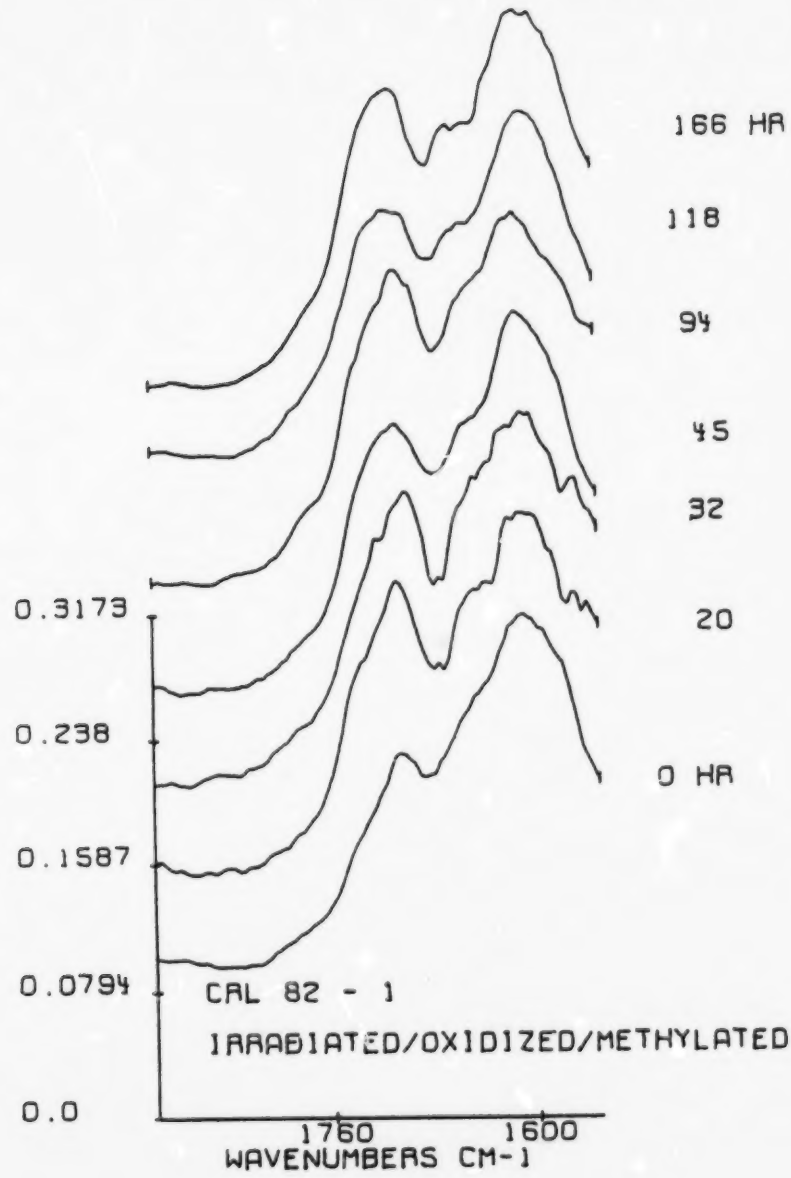

166 HR
118
94
45
32
20
0 HR
0.3173
0.238
0.1587
0.0794
0.0
CAL 82 - 1
IRRADIATED/OXIDIZED/METHYLATED
1760
1600
WAVENUMBERS CM-1

FIGURE 74

DIFFERENCE SPECTRUM
CRL 82 - 1
IRRADIATED/OXIDIZED. THEN METHYLATED
20 HR MINUS 0 HR

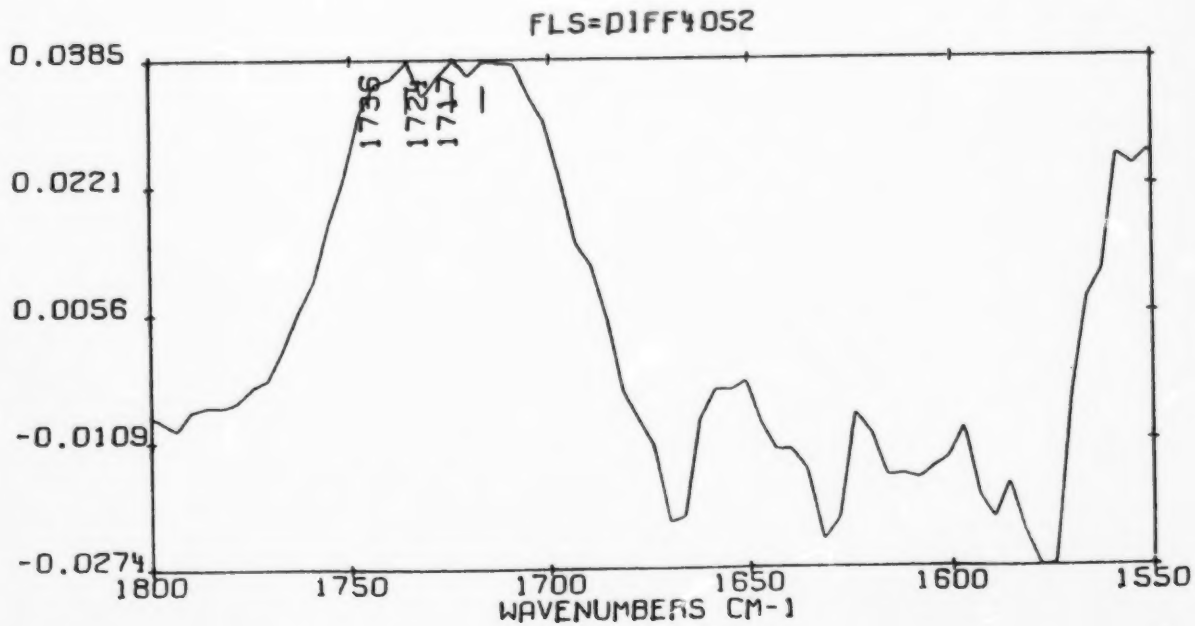


FIGURE 75

DIFFERENCE SPECTRUM

CRL 82 - 1 IRRADIATED/OXIDIZED THEN METHYLATED

32 HR MINUS ZERO HR

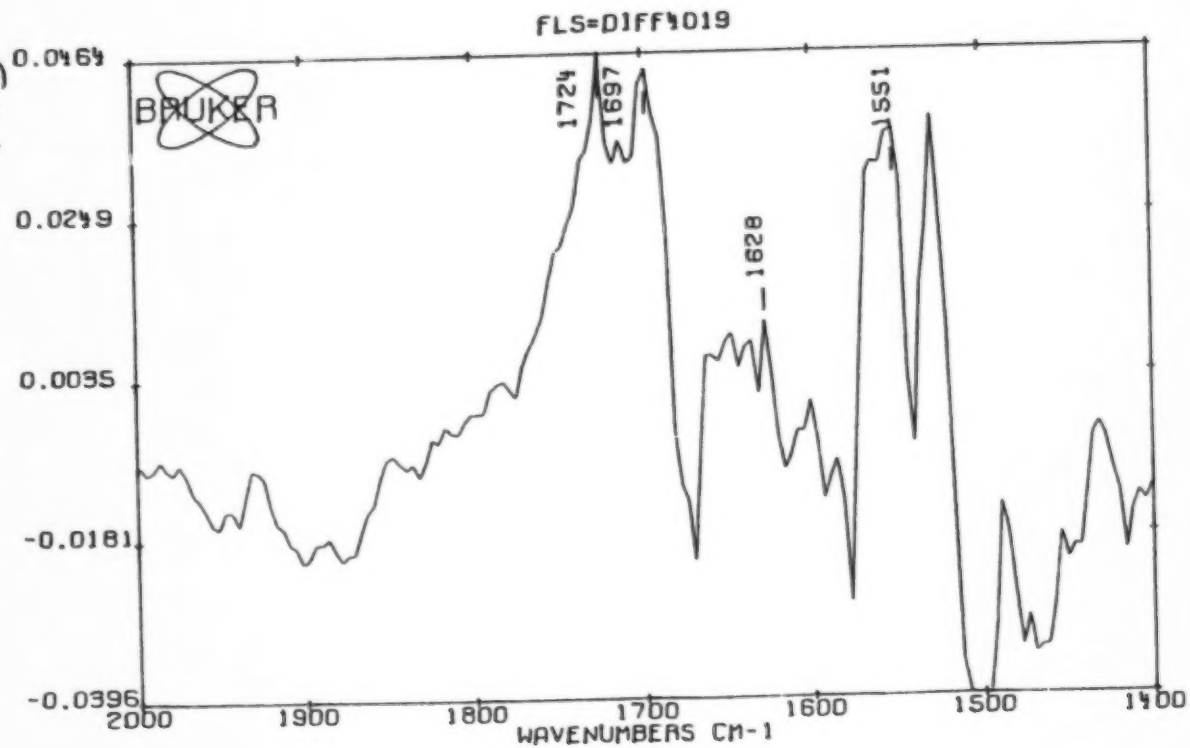


FIGURE 76

DIFFERENCE SPECTRUM

CRL 82 - 1

IRRADIATED/OXIDIZED THEN METHYLATED

45 HR MINUS 0 HR

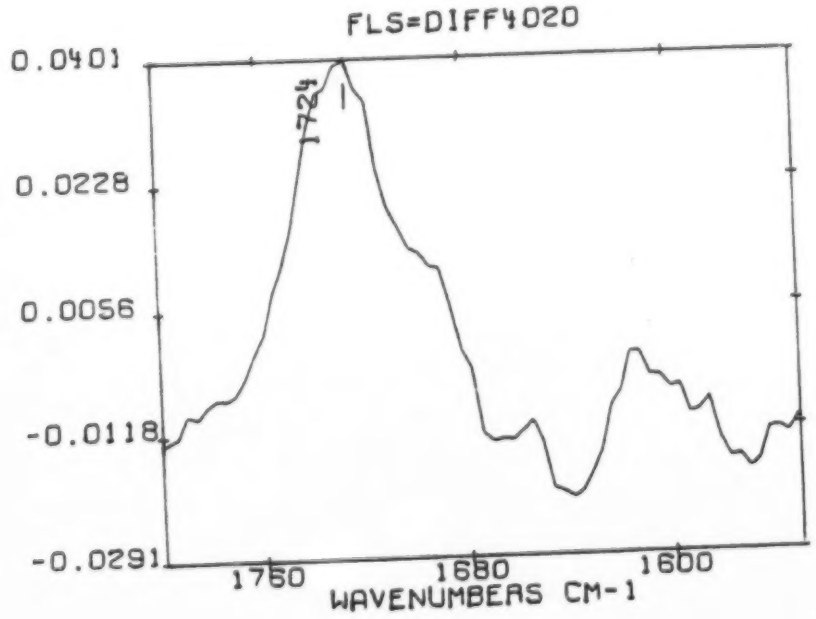


FIGURE 77

DIFFERENCE SPECTRUM
CRL 82 - 1
IRRADIATED OXIDIZED, THEN METHYLATED
94 HR MUNUS 0 HR

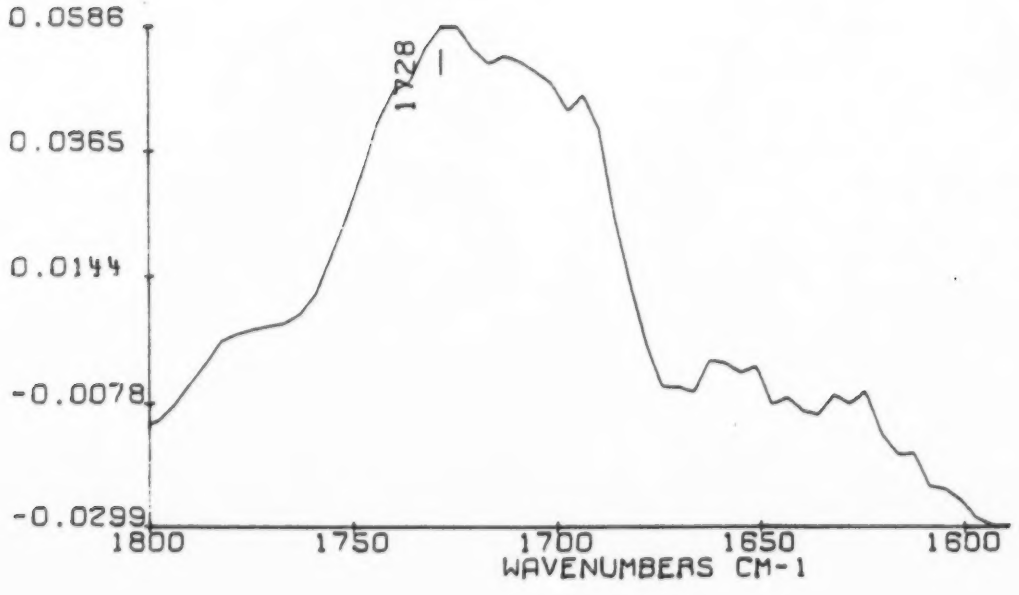


FIGURE 78

DIFFERENCE SPECTRUM
CRL 82 - 1
IRRADIATED/OXIDIZED THEN METHYLATEI
118 HR MINUS 0 HR

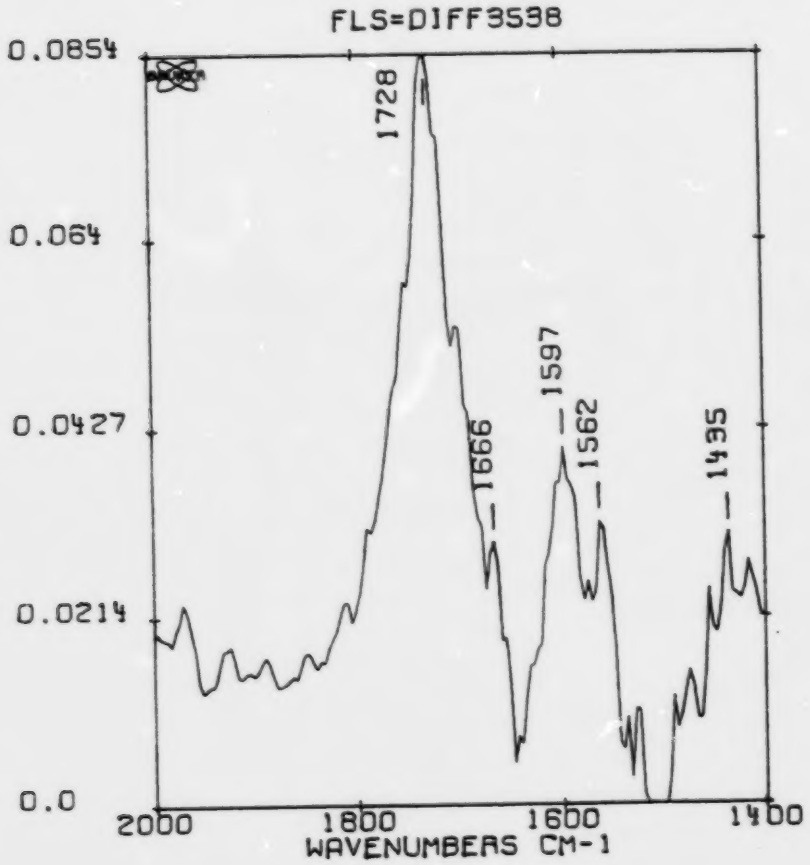


FIGURE 79

DIFFERENCE SPECTRUM
COAL CRL 82 - 1
IRRADIATED/OXIDIZED/METHYLATED
166 HR MINUS 0 HR

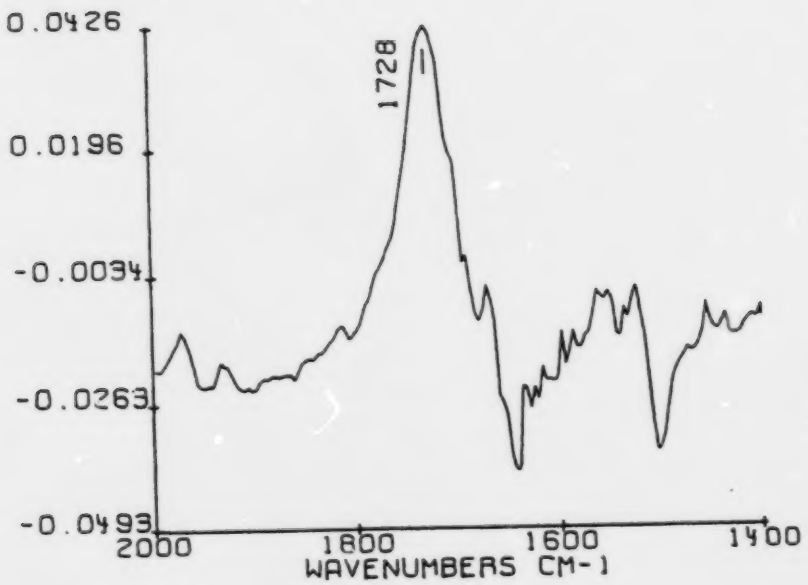


FIGURE 80

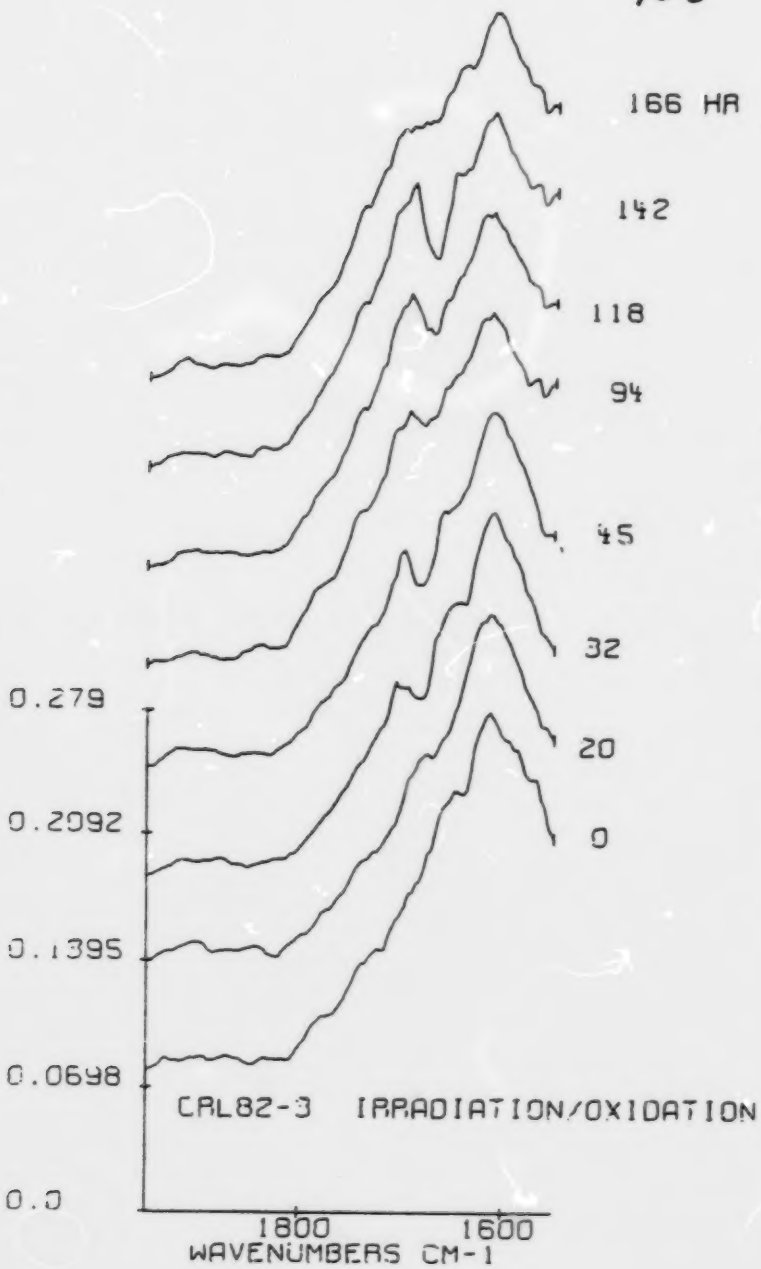

166 HR
142
118
94
45
32
20
0
0.279
0.2092
0.1395
0.0698
0.0
CRL82-3 IRRADIATION/OXIDATION
1800
1600
WAVENUMBERS CM-1

FIGURE 81

DIFFERENCE SPECTRA

CRL 82-3

IRRADIATED 32 H VS. FRESH

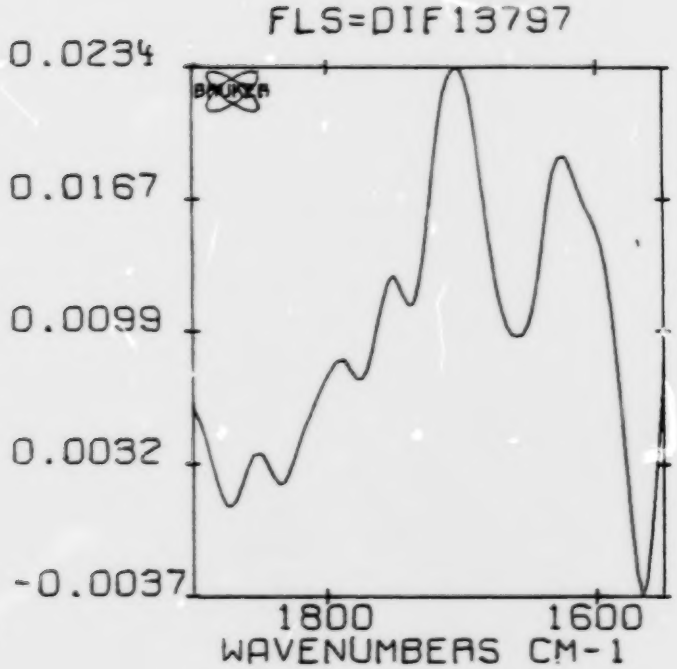


FIGURE 82

DIFFERENCE SPECTRA

CRL 82-3

IRRADIATED 94 H VS. FRESH

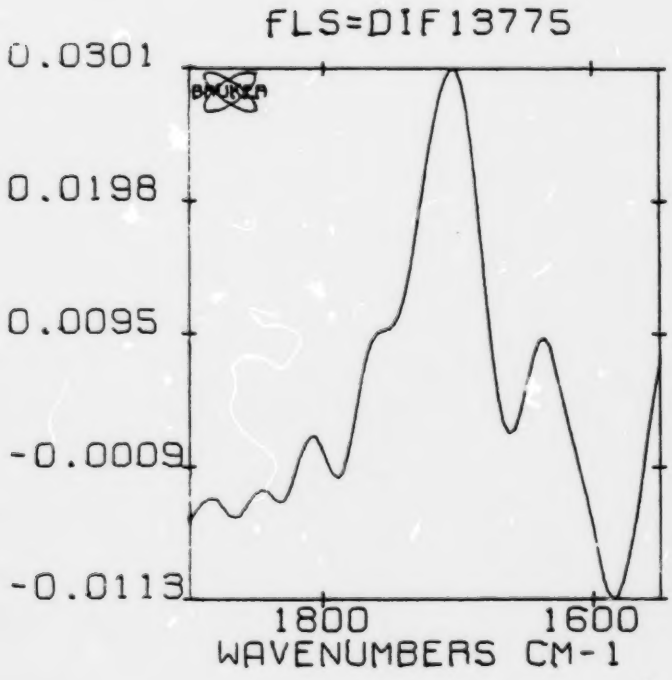


FIGURE 83

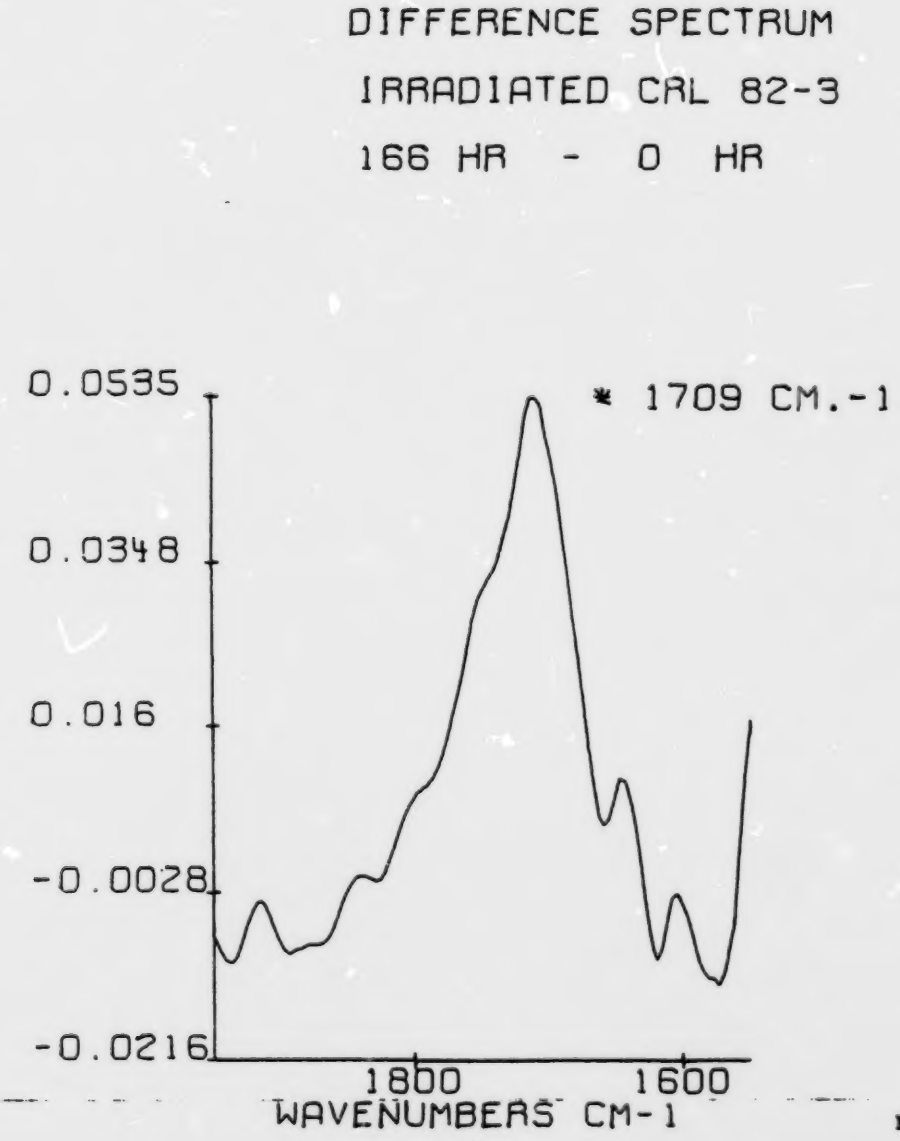

DIFFERENCE SPECTRUM
IRRADIATED CRL 82-3
166 HR - 0 HR
0.0535
0.0348
0.016
-0.0028
-0.0216
* 1709 CM.-1
1800
1600
WAVENUMBERS CM-1

FIGURE 84

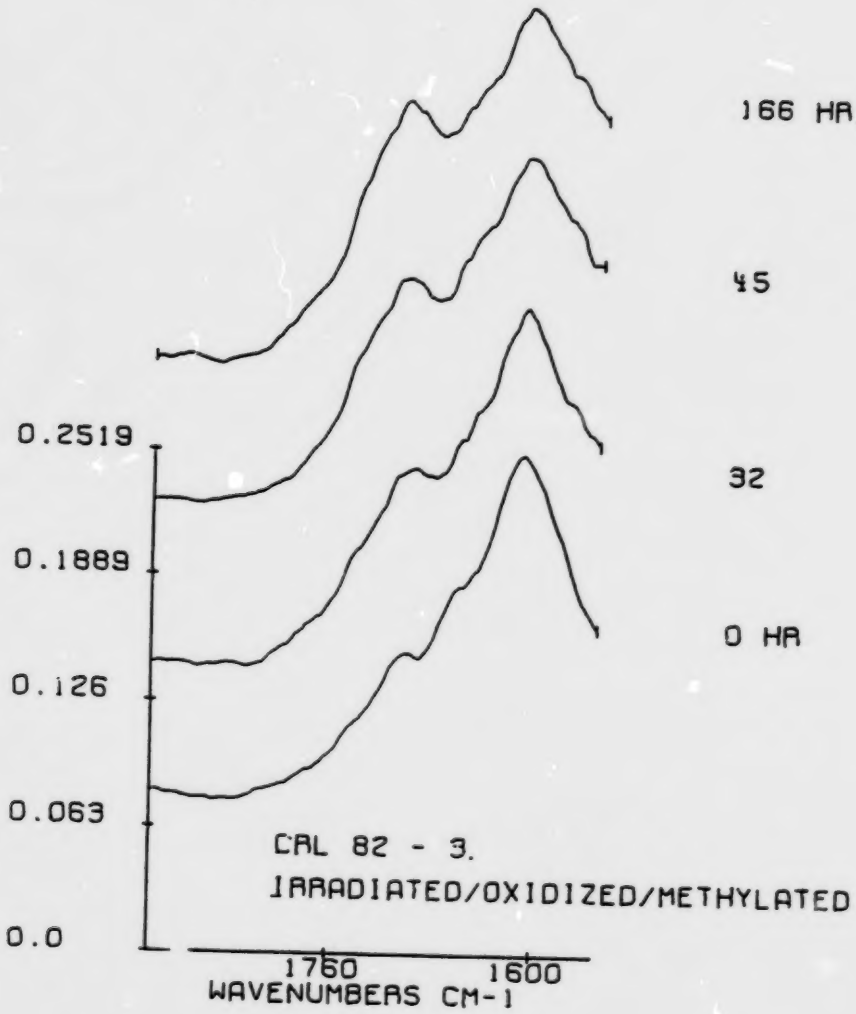

166 HR
45
32
0 HR
0.2519
0.1889
0.126
0.063
0.0
CAL 82 - 3.
IRRADIATED/OXIDIZED/METHYLATED
1760
1600
WAVENUMBERS CM-1

FIGURE 85

CAL 82- 3 DIFFERENCE SPECTRUM
METHYLATED/IRRADIATED/OXIDIZED
45 HR - 0 HR

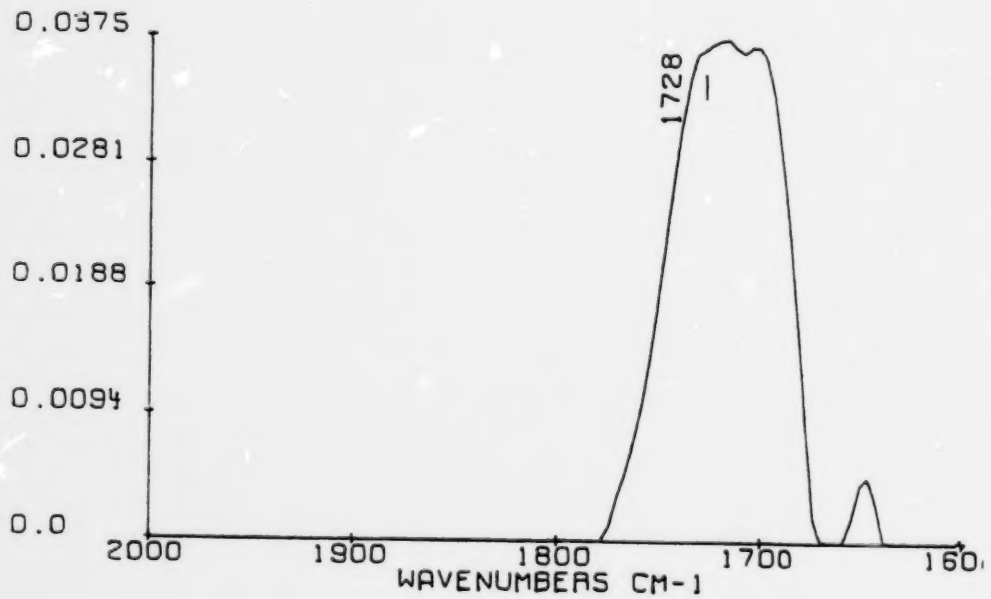


FIGURE 86

CAL 82- 3

DIFFERENCE SPECTRUM
METHYLATED/IRRADIATED/OXIDIZED
166 HR - 0 HR

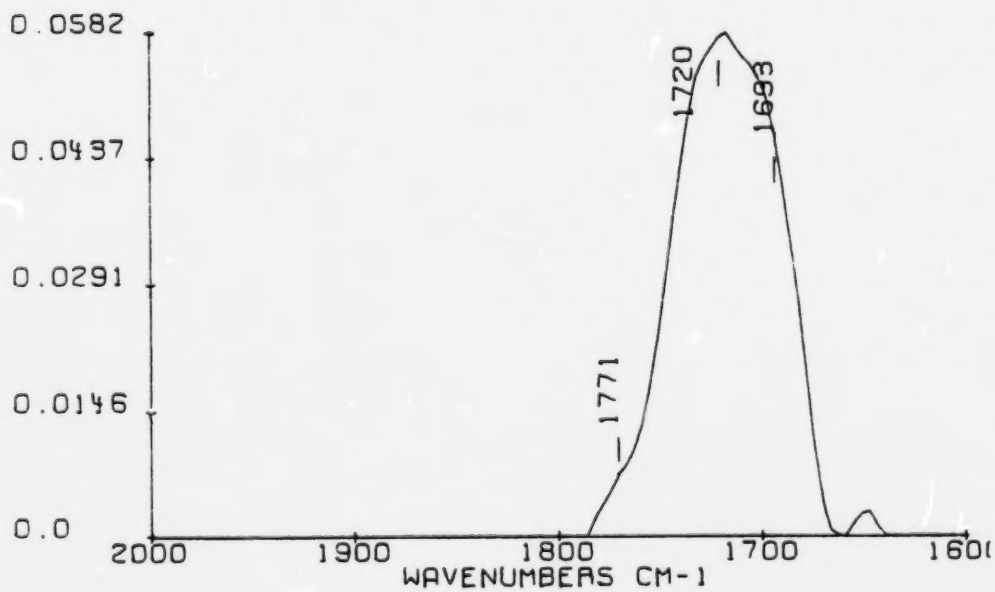
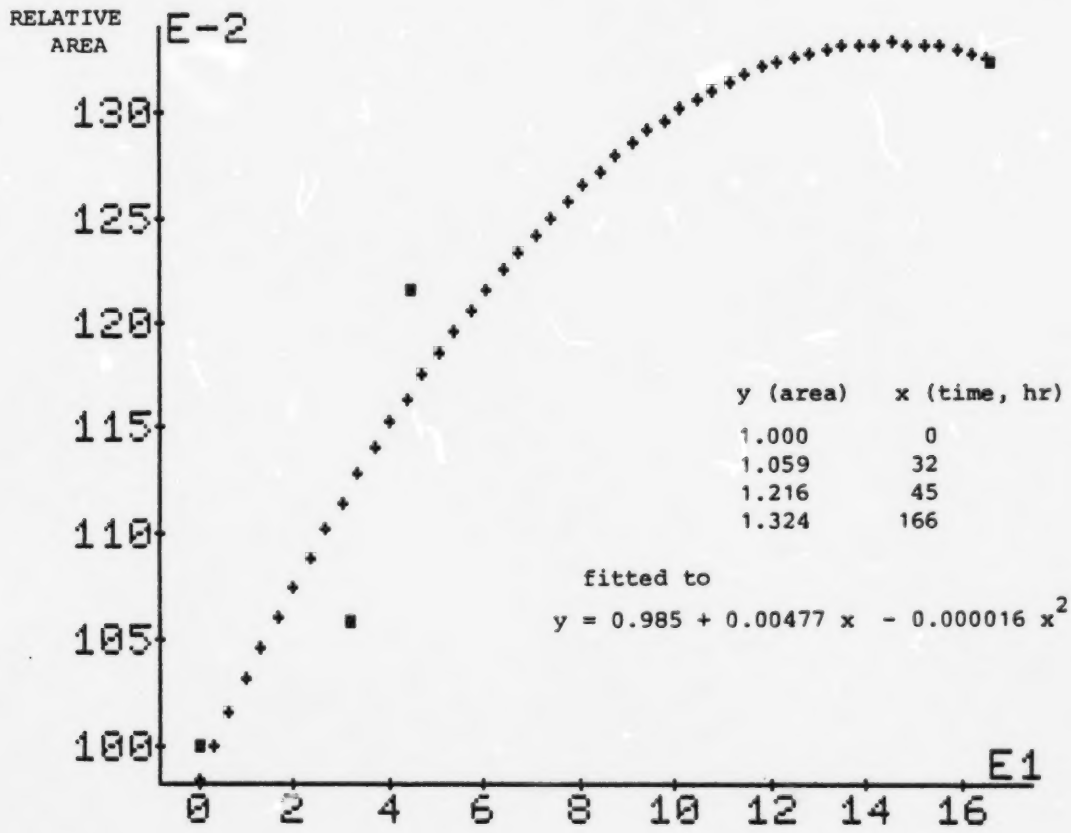


FIGURE 87



TIME OF IRRADIATION (hr/10 units)

FIGURE 88

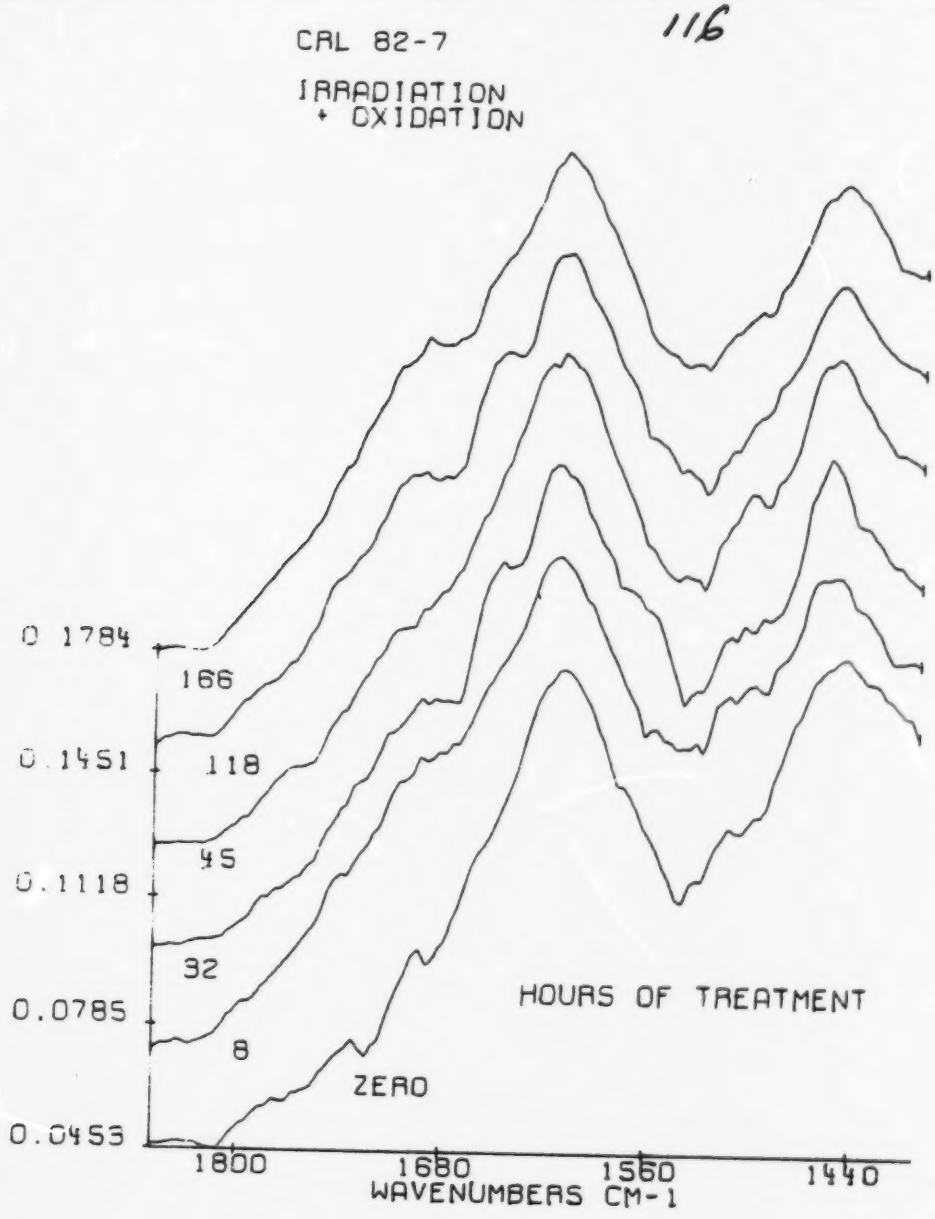

CRL 82-7
IRRADIATION
+ OXIDATION
0.1784
166
0.1451
118
45
0.1118
32
0.0785
8
ZERO
0.0453
HOURS OF TREATMENT
1800
1680
1560
1440
WAVENUMBERS CM-1

FIGURE 89

DIFFERENCE SPECTRUM
IRRADAITED CRL 82 - 7
166 HR - 0 HR

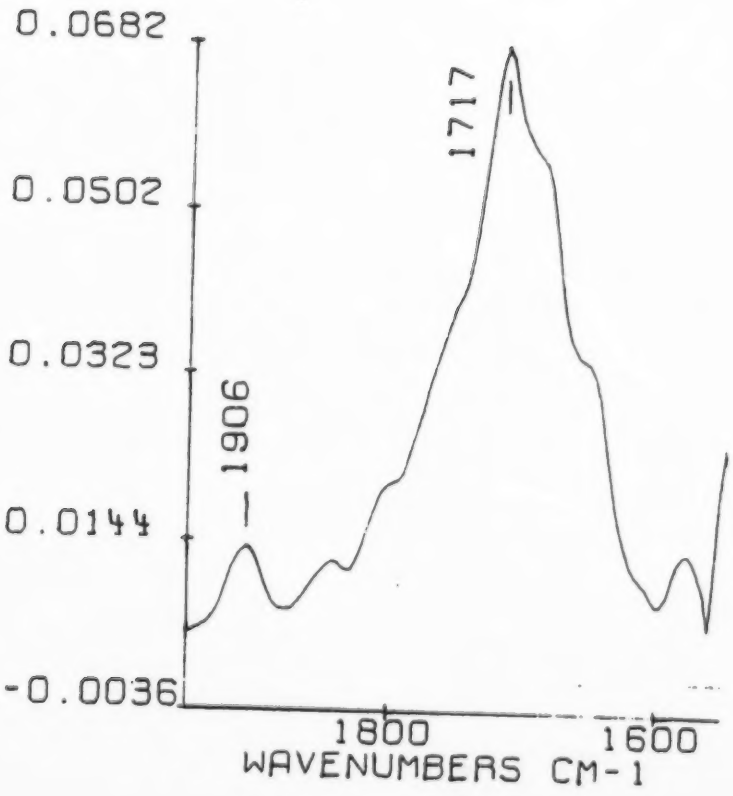


FIGURE 90

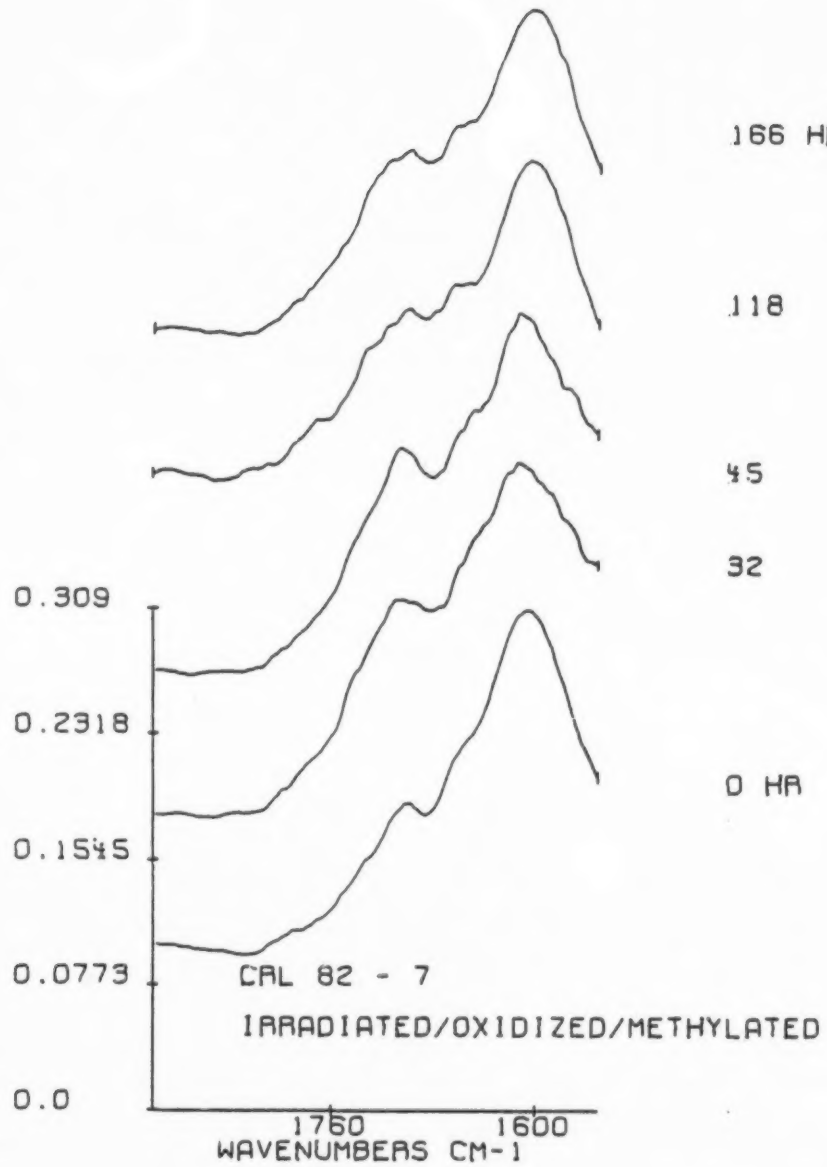

166 HR
118
45
32
0 HR
0.309
0.2318
0.1545
0.0773
0.0
CAL 82 - 7
IRRADIATED/OXIDIZED/METHYLATED
1760
1600
WAVENUMBERS CM-1

FIGURE 91

DIFFERENCE SPECTRUM
CRL 82 - 7
METHYLATED/OXIDIZED/IRRADIATED
32 HR - 0 HR

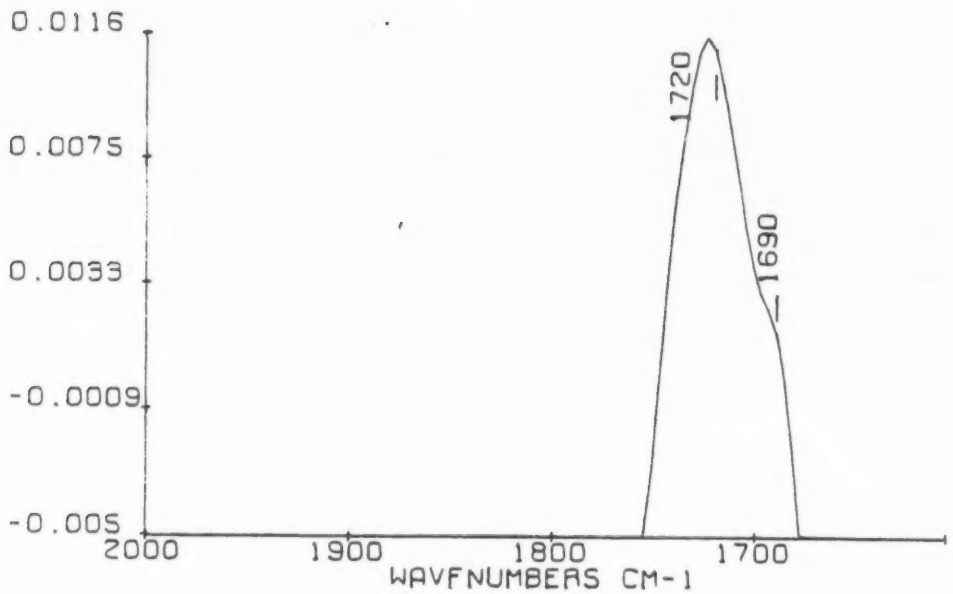


FIGURE 92

DIFFERENCE SPECTRUM
METHYLATED IRRADIATED CRL-82-7
166 HR - 0 HR

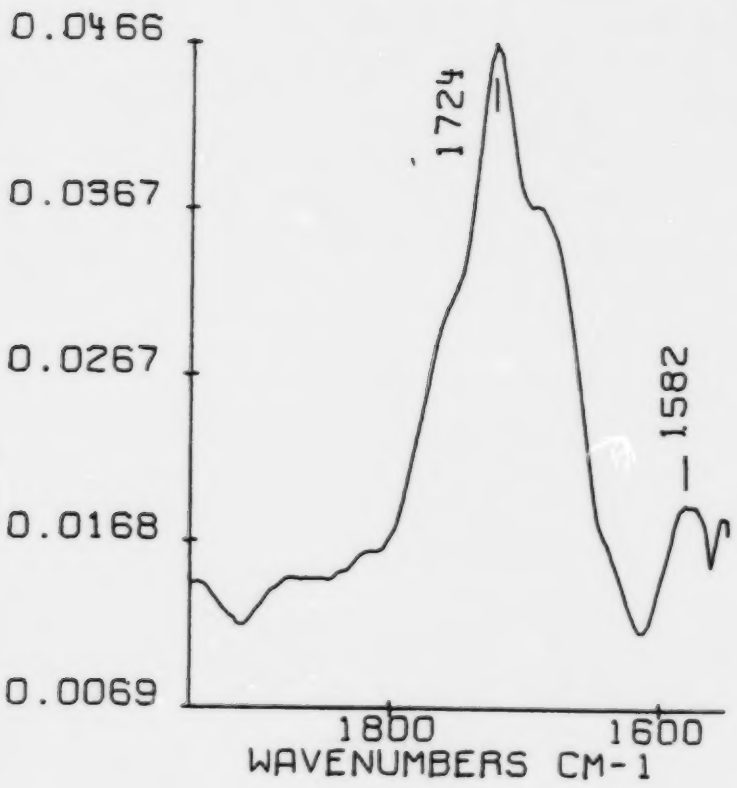
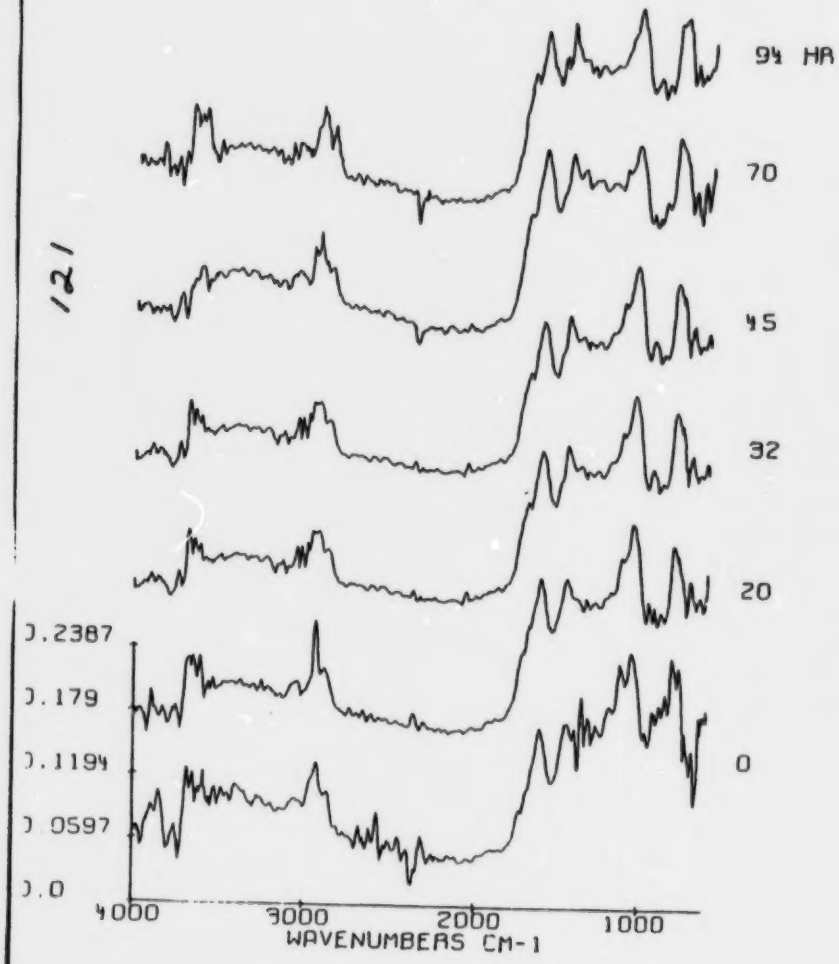


FIGURE 93



CRL 82 - 8
IRRADIATION/OXIDATION

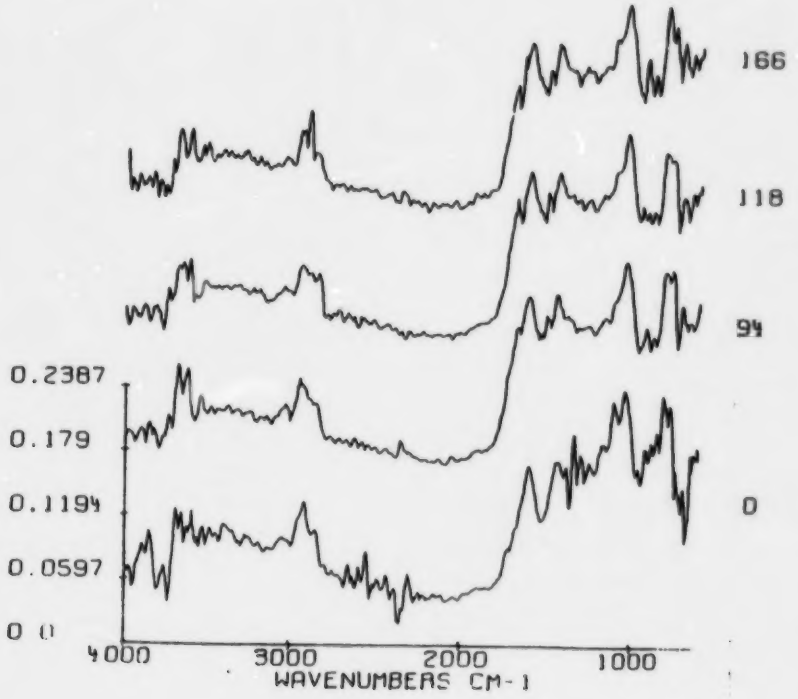


FIGURE 94

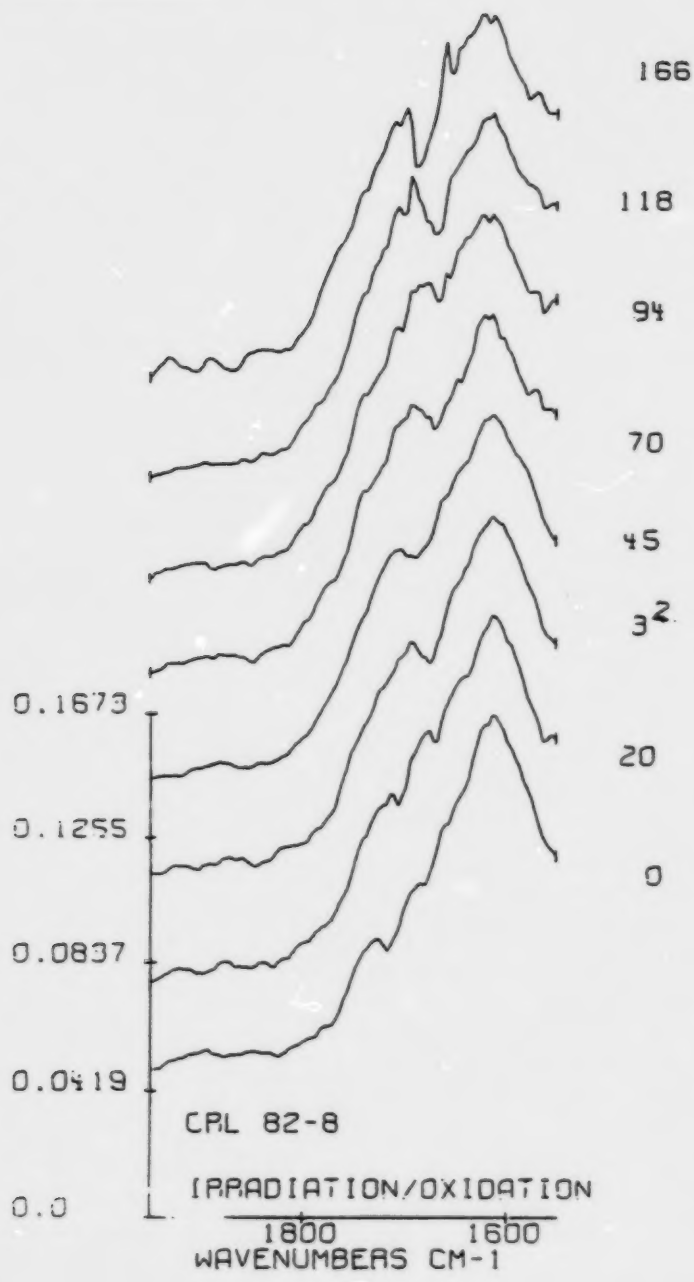

166 HR
118
94
70
45
32
20
0
0.1673
0.1255
0.0837
0.0419
0.0
CRL 82-8
IRRADIATION/OXIDATION
1800
1600
WAVENUMBERS CM-1

FIGURE 95

DIFFERENCE SPECTRUM
IRRADIATED CRL 82-8
166 HR - 0 HR

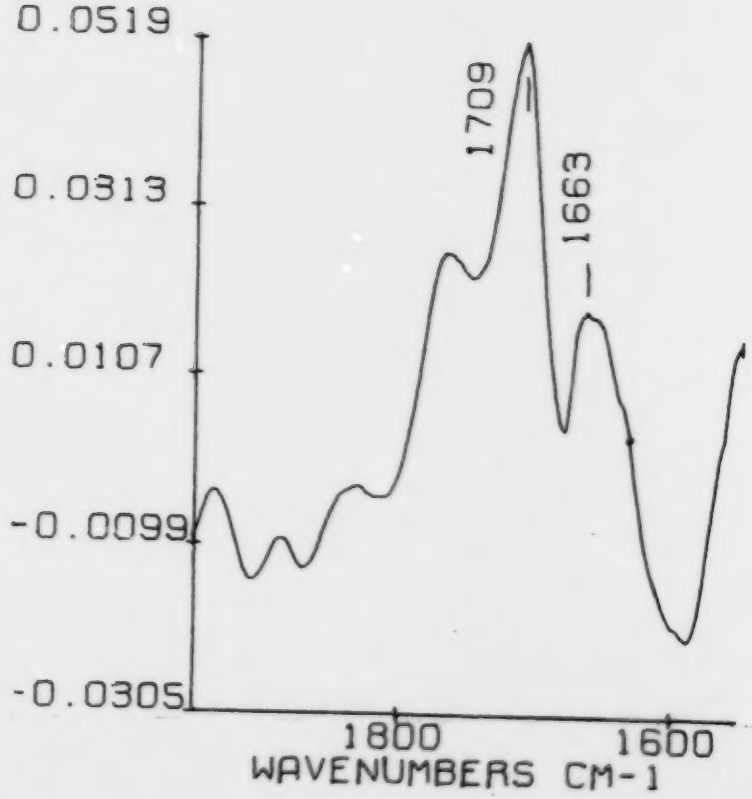


FIGURE 96

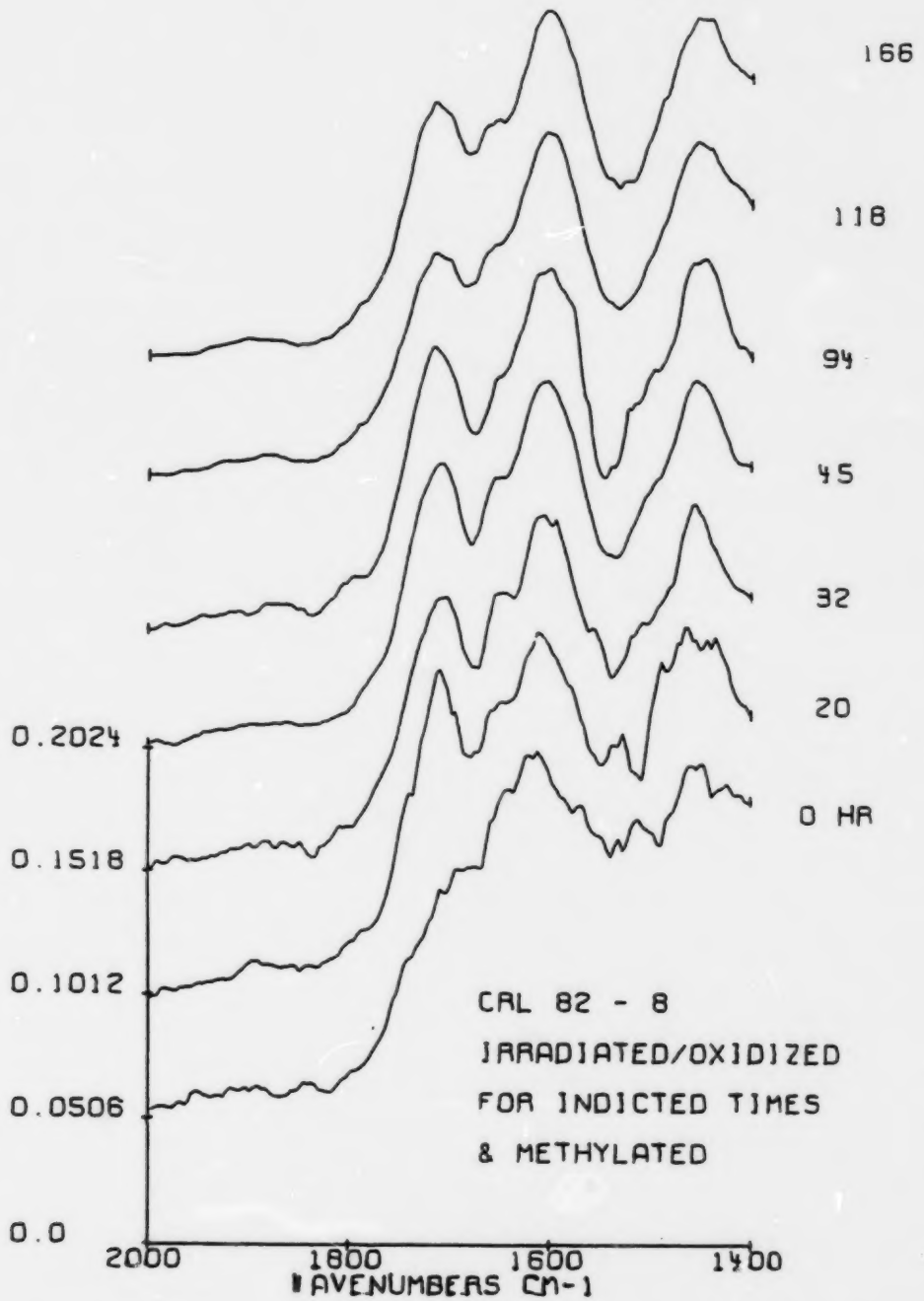

166
118
94
45
32
20
0 HR
0.2024
0.1518
0.1012
0.0506
0.0
2000
1800
1600
1400
WAVENUMBERS CM-1
CRL 82 - 8
IRRADIATED/OXIDIZED
FOR INDICTED TIMES
& METHYLATED

FIGURE 97

DIFFERENCE SPECTRUM

METHYLATED IRRADIATED CRL-82-8

166HR - 0 HR

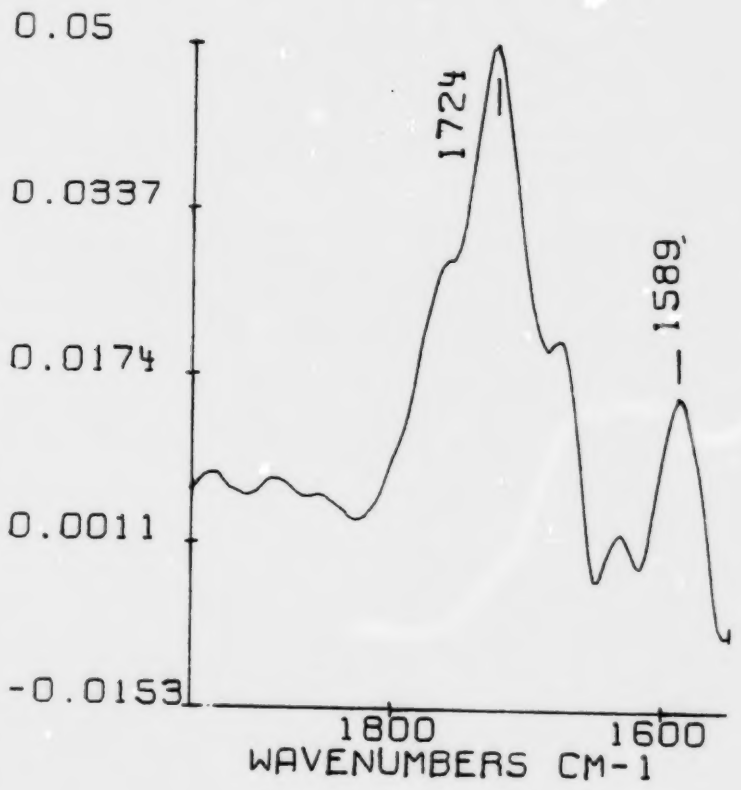


FIGURE 98

DIFFERENCE SPECTRUM
IRRADIATED CRL 82- 9
166 HR - 0 HR

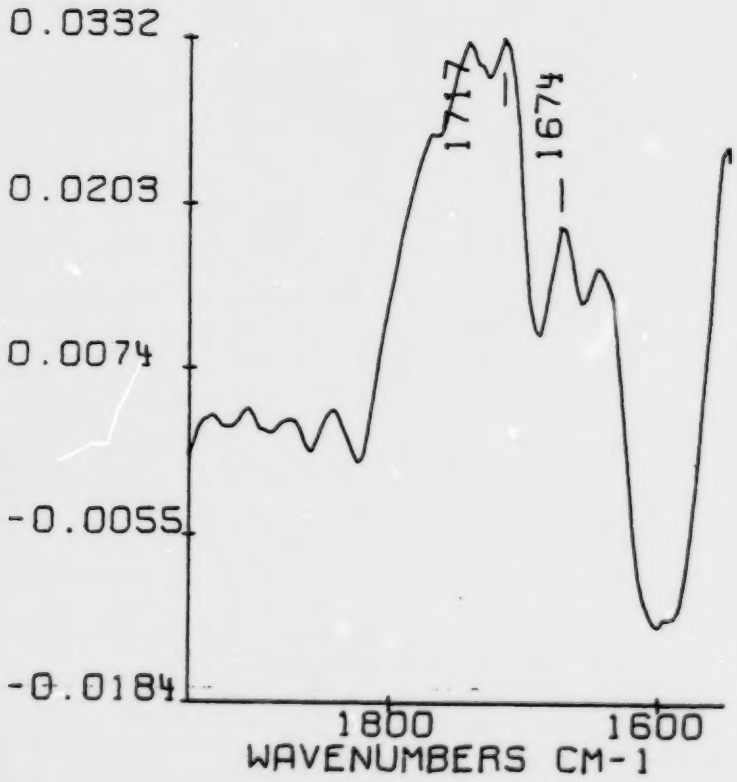


FIGURE 99

DIFFERENCE SPECTRUM

METHYLATED IRRADIATED CRL-82 -9

166 HR -0 HR

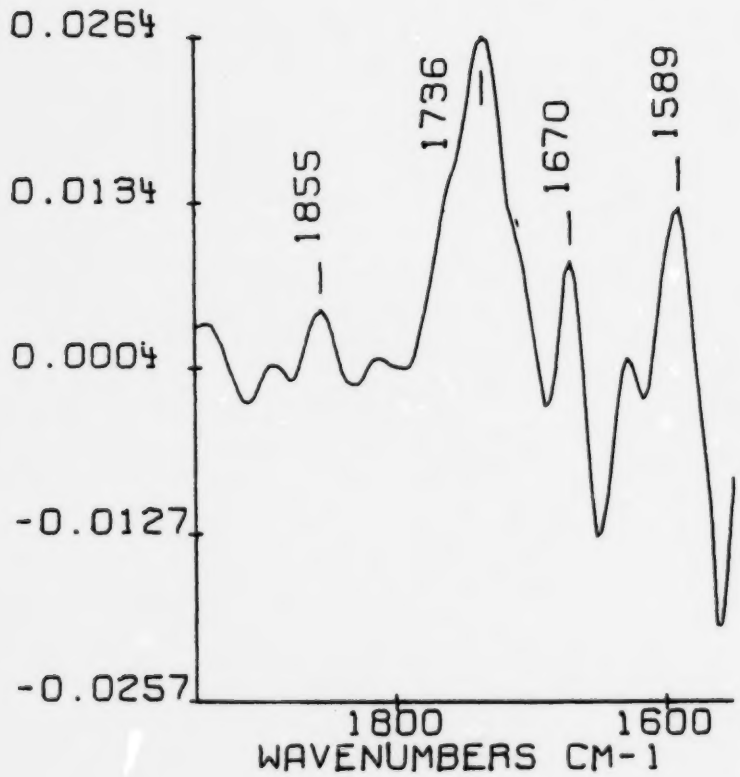
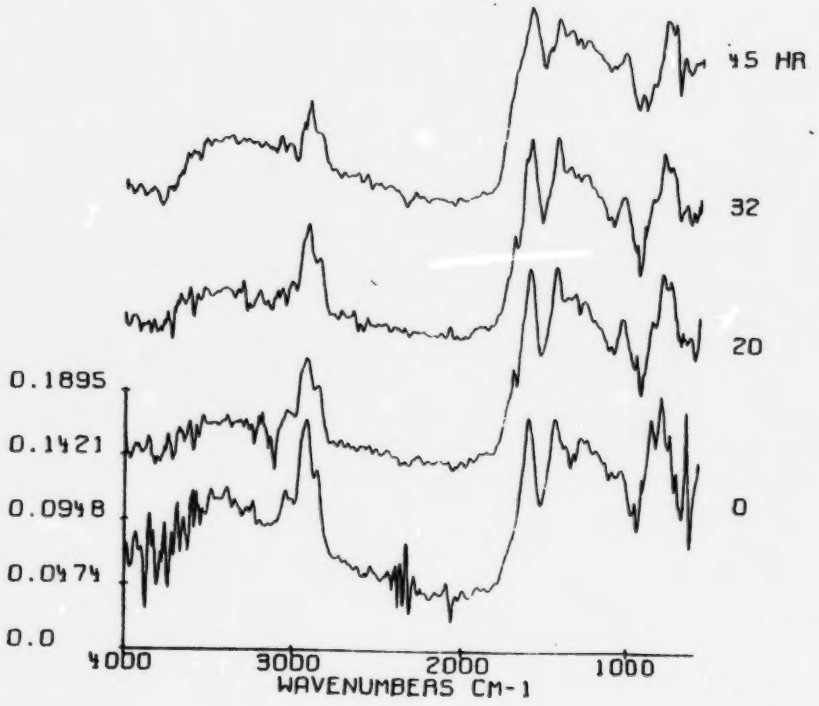


FIGURE 100

CAL 82-10

IRRADIATION/OXIDATION



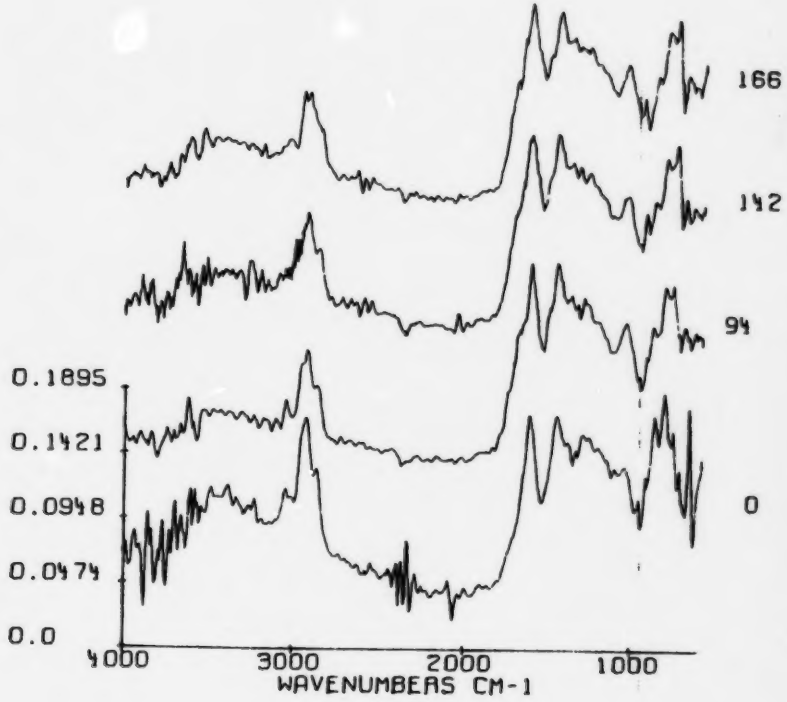


FIGURE 101

DIFFERENCE SPECTRUM
IRRADIATED CRL 82 - 10
32 HR - 0 HR

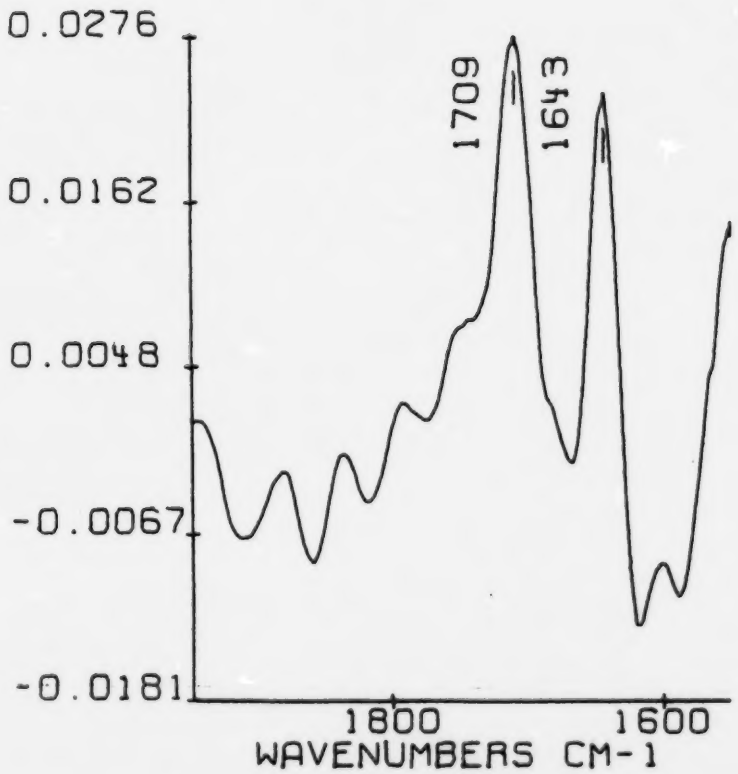


FIGURE 102

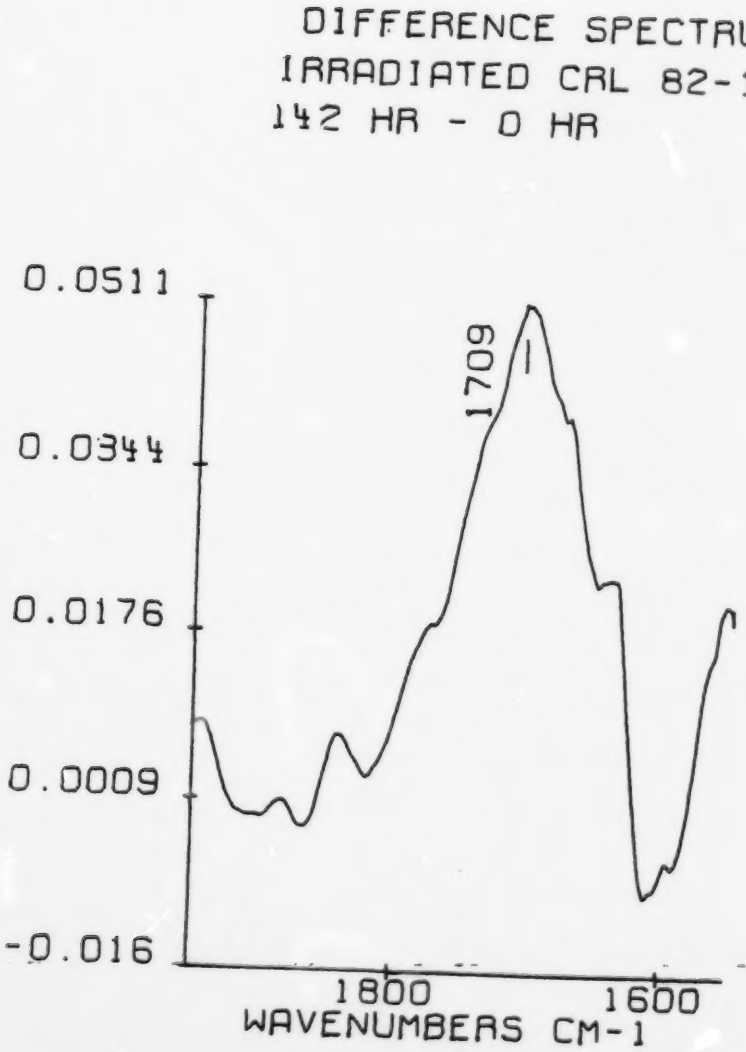

DIFFERENCE SPECTRUM
IRRADIATED CRL 82-10
142 HR - 0 HR
0.0511
0.0344
0.0176
0.0009
-0.016
1709
1800
1600
WAVENUMBERS CM-1

FIGURE 103

DIFFERENCE SPECTRUM
IRRADIATED CRL 82-10
166 HR - 0 HR

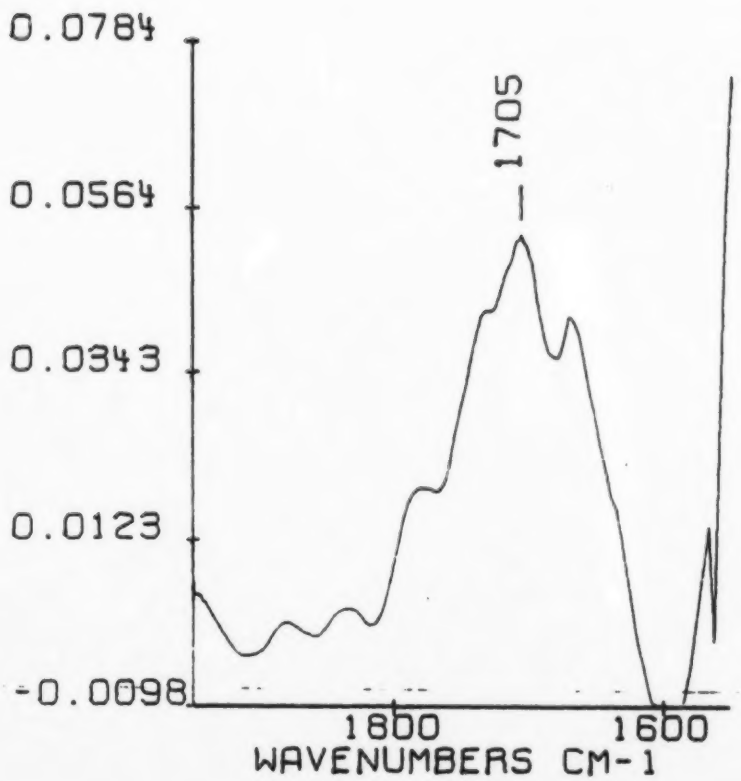


FIGURE 104

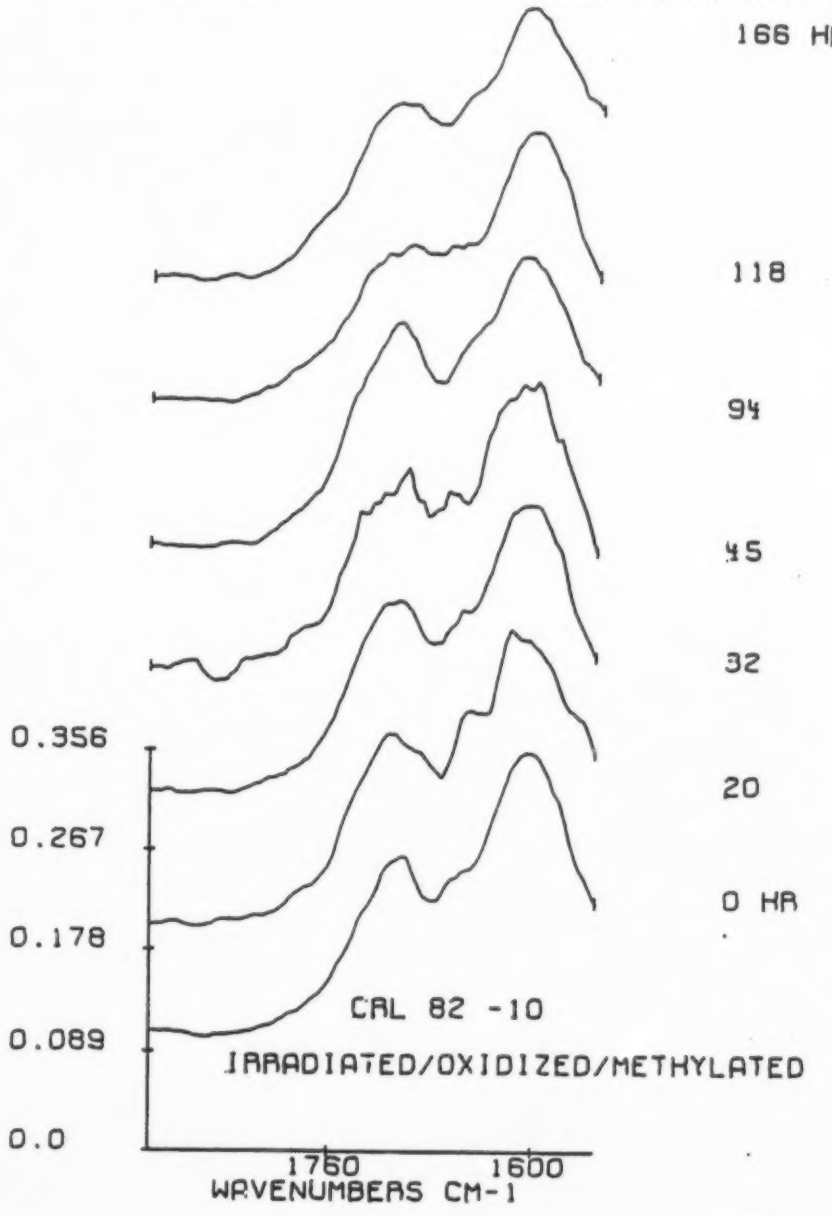

166 HR
118
94
45
32
20
0 HR
0.356
0.267
0.178
0.089
0.0
CAL 82 -10
IRRADIATED/OXIDIZED/METHYLATED
1760
1600
WAVENUMBERS CM-1

FIGURE 105

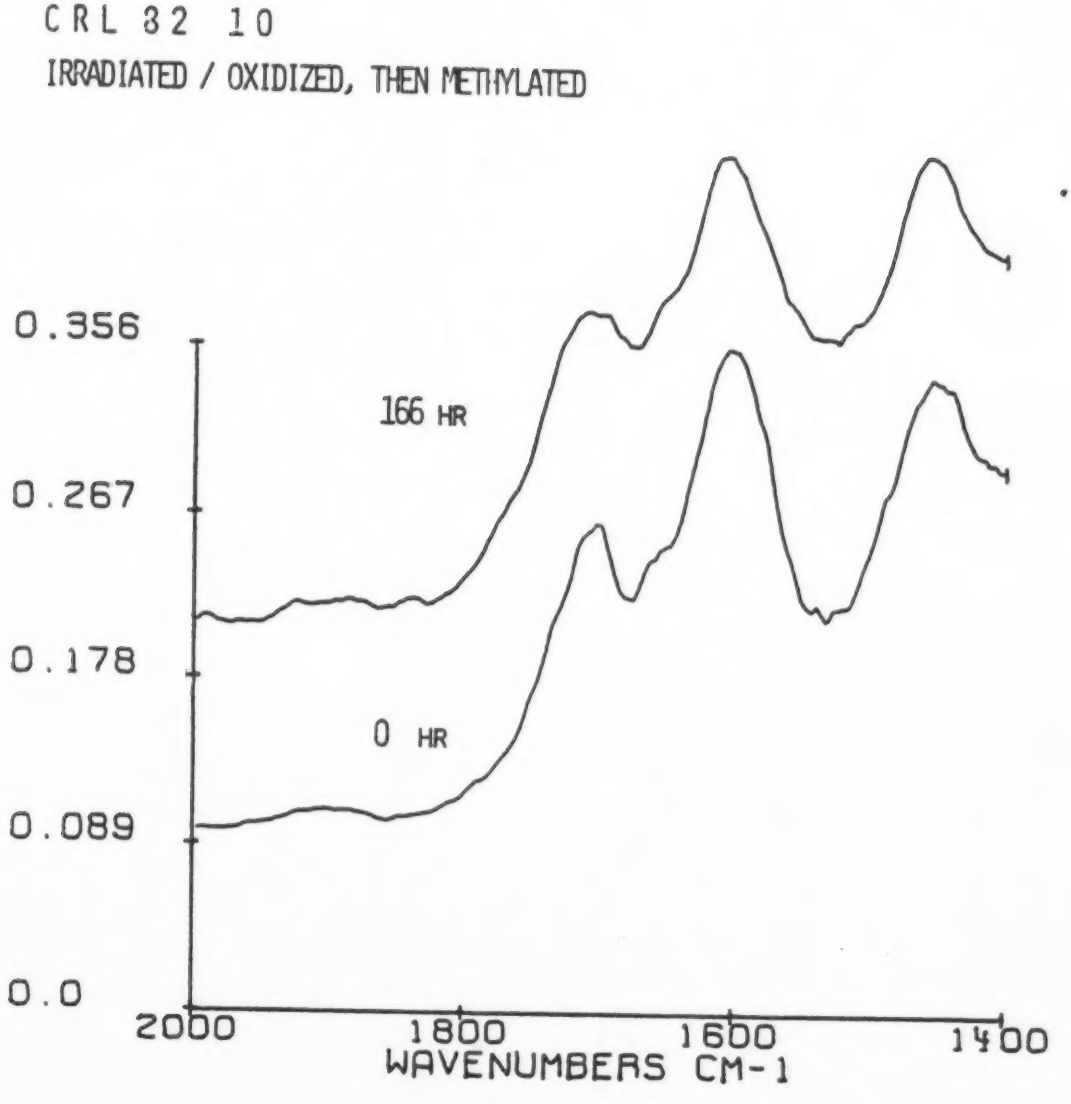
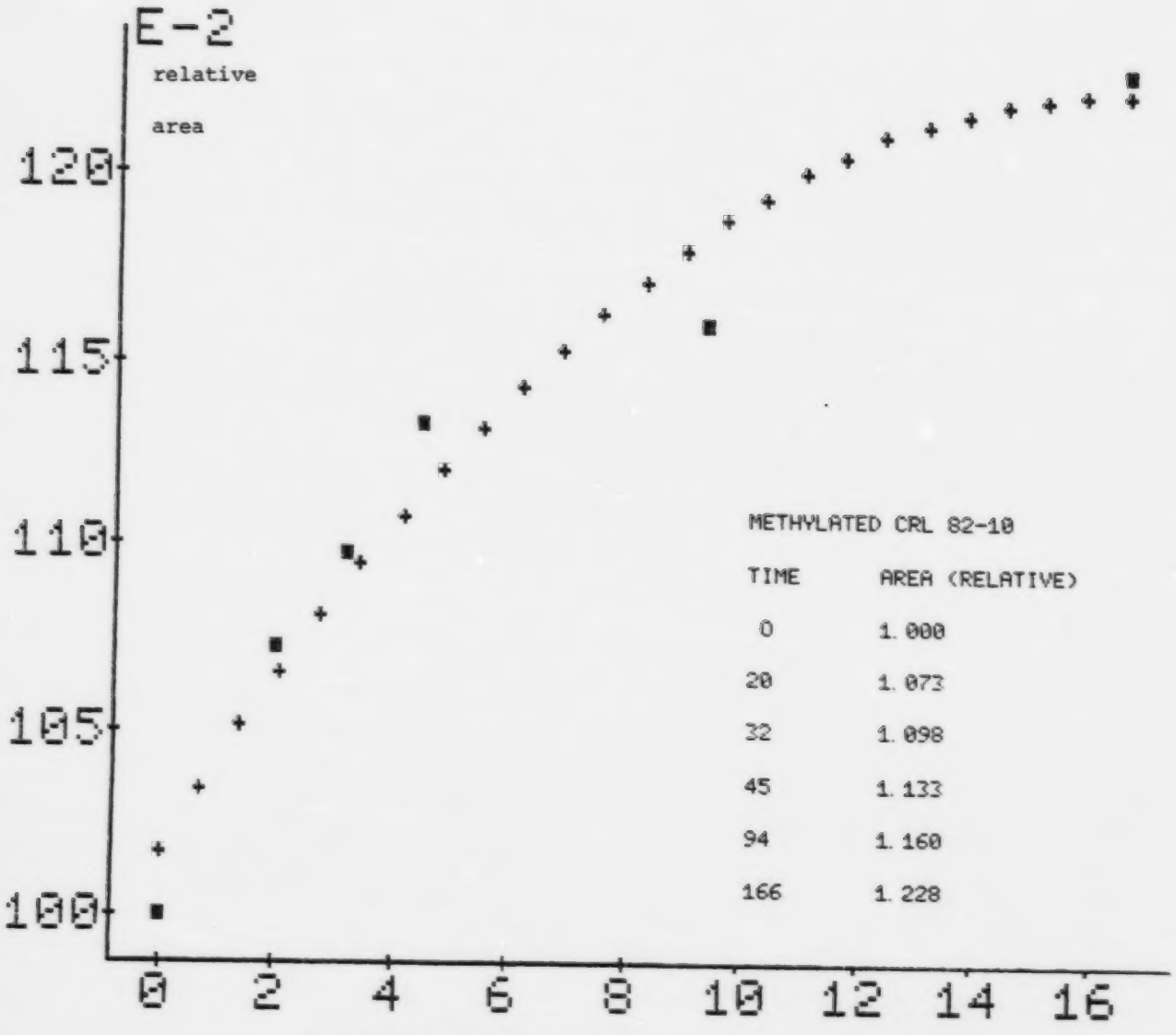

CRL 32 10
IRRADIATED / OXIDIZED, THEN METHYLATED
0.356
0.267
0.178
0.089
0.0
166 HR
0 HR
2000
1800
1600
1400
WAVENUMBERS CM-1

FIGURE 106



METHYLATED CRL 82-10

TIME	AREA (RELATIVE)
0	1.000
20	1.073
32	1.098
45	1.133
94	1.160
166	1.228

FIGURE 107

COALS OXIDIZED
@ 300 DEG. C
FOR 30 MIN.

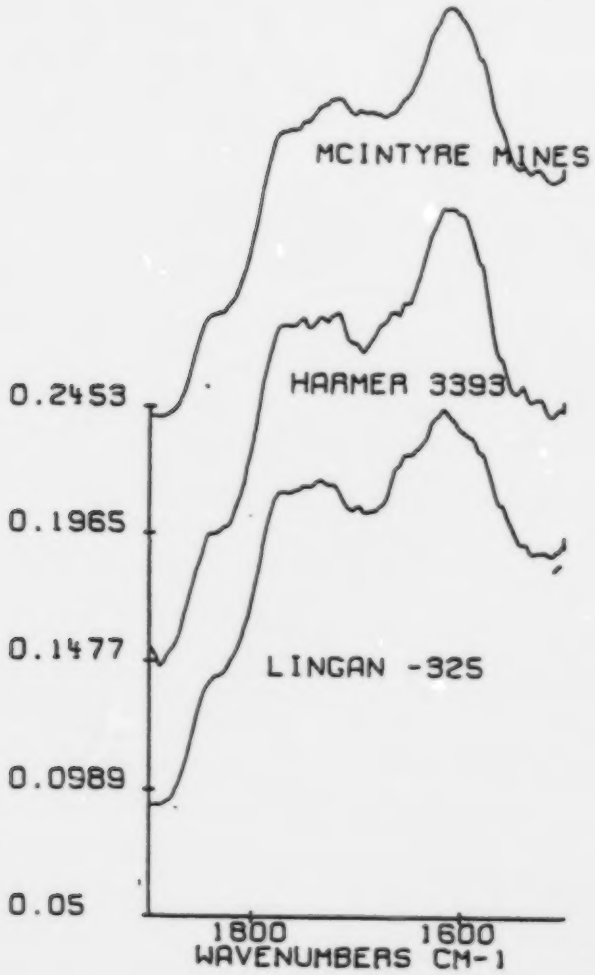


FIGURE 108

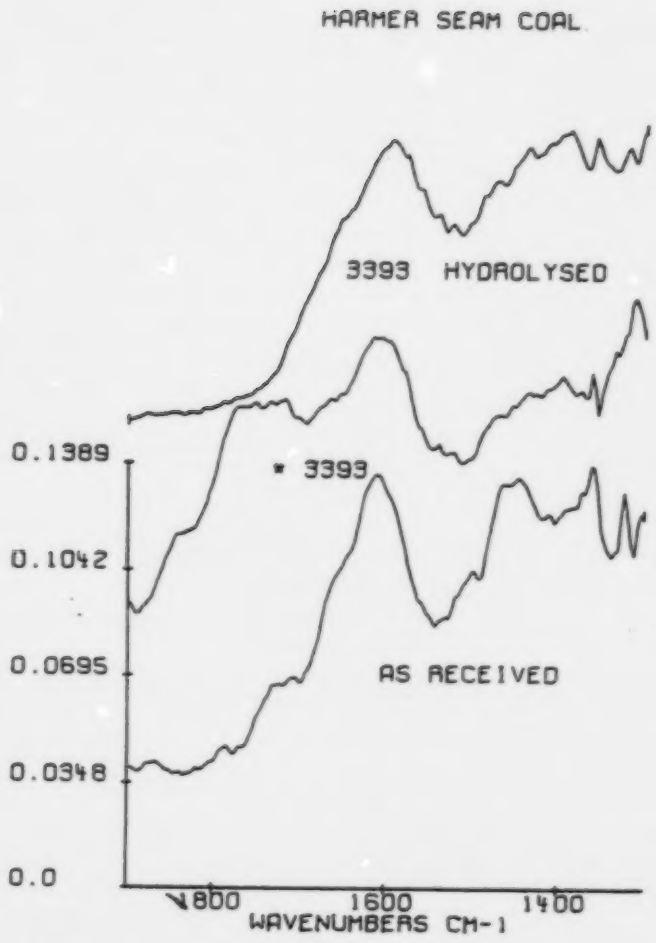

HARMER SEAM COAL
3393 HYDROLYSED
* 3393
AS RECEIVED
0.1389
0.1042
0.0695
0.0348
0.0
1800
1600
1400
WAVENUMBERS CM-1

FIGURE 109

HARMER SEAM COAL

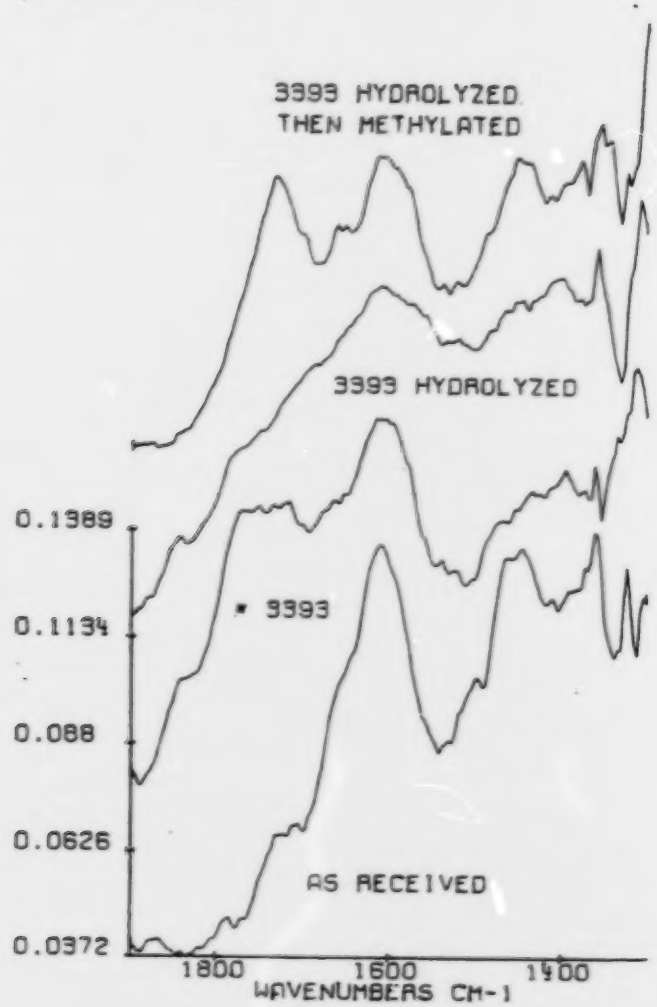


FIGURE 110

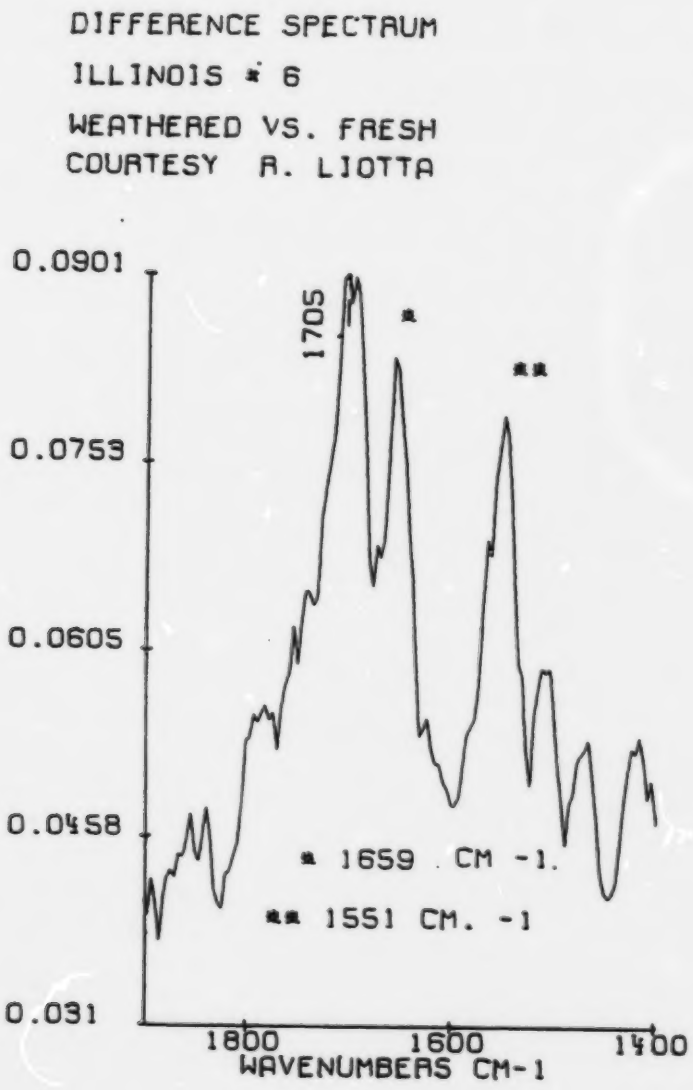

DIFFERENCE SPECTRUM
ILLINOIS # 6
WEATHERED VS. FRESH
COURTESY R. LIOTTA
0.0901
0.0753
0.0605
0.0458
0.031
1705
* 1659 CM -1.
** 1551 CM. -1
1800
1600
1400
WAVENUMBERS CM-1

FIGURE 111

DIFFERENCE SPECTRUM
METHYLATED ILLINOIS # 6
WEATHERED VS. FRESH
(COURTESY R. LIOTTA)

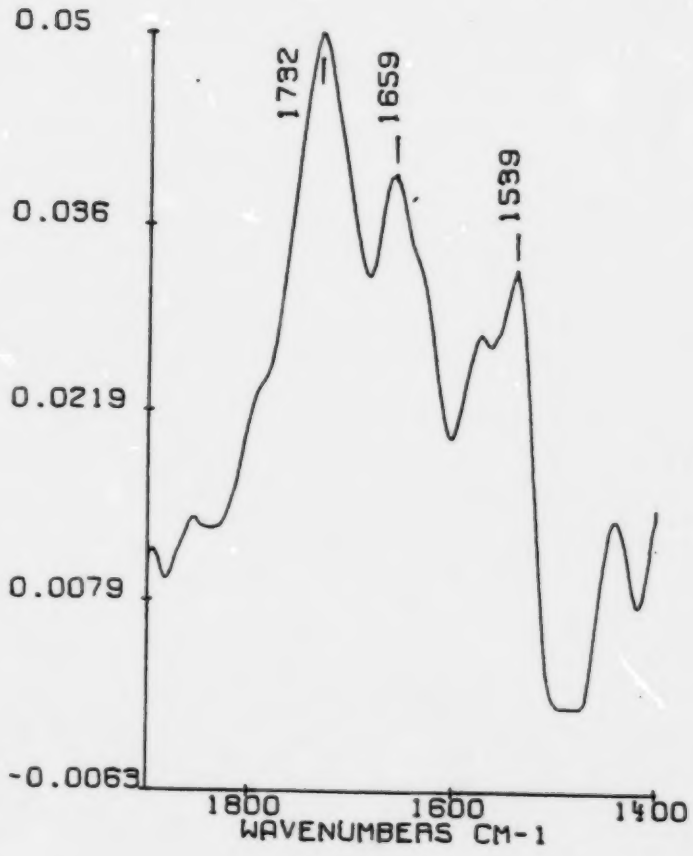


FIGURE 112

CONCLUSIONS

It is evident from the cited results in this report that photoacoustic infrared Fourier Transform (PAIFT) spectroscopy has the capabilities of providing rapid and sensitive indicators of the extent, nature, and pathways of coal oxidation. Routine or service measurements are practicable, and the high sensitivity of PAIFT spectra to oxidation offers unique opportunities. It also seems that rapid analyses of mineral-matter profiles in coal samples may be achieved using PAIFT techniques. It is emphasized that the successes reported here are a consequence of the particular configuration of basic FTIR system and photoacoustic accessory system, and should not be taken as a blanket recommendation for the interfacing of the present photoacoustic detector to other types of FTIR spectrometer.

With further developments, particularly with more intense light sources and a more sensitive photoacoustic detector, it would seem that PAIFT could become the accessory technique of choice for examination of hitherto intractable samples.

ACKNOWLEDGEMENTS

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